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National Dioxin Study Tier 4
Combustion Sources
Quality Assurance Project Plan

Radian Corp., Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Jun 85

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16. ABSTRACT

The objective of Tier 4 of the National Dioxin Study is to determine if combustion devices are significant sources of dioxin emissions. This project plan describes the quality assurance and quality control activities associated with emission tests to be conducted at twelve (12) sites. The tests will involve determination of of dioxin concentrations and mass flow rates at the outlet of the combustion device and/or any air pollution control equipment. Flue gas combustion parameters (CO, CO_2, O_2, SO_2, NO_x, and total Hydrocarbons) will be monitored and samples for dioxin precursor analysis will be collected. Equipment calibration, sample custody, data reduction, and reporting requirements are discussed.

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Quality Assurance Project Plan

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National Dioxin Study Tier 4 — Combustion Sources

Quality Assurance Project Plan

By
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Research Triangle Park, NC 27709

Contract No. 68-02-3513
And
Contract No. 68-03-3148

EPA Project Officers:
William H. Lamason (OAQPS)
And
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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, NC 27711
June 1985

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5	LABORATORY ANALYTICAL PROCEDURES	11	1	4/5/85
6	SAMPLE CUSTODY	16	1	4/5/85
7	CALIBRATION PROCEDURES	15	2	4/5/85
8	DATA REDUCTION, VALIDATION, AND REPORTING	11	2	4/5/85
9	INTERNAL QUALITY CONTROL CHECKS	21	2	4/5/85
10	PERFORMANCE AND SYSTEMS AUDITS	6	1	4/5/85
11	PREVENTIVE MAINTENANCE	1	0	4/5/85
12	ASSESSMENT OF PRECISION, ACCURACY AND COMPLETENESS	2	1	4/5/85
13	CORRECTIVE ACTION	2	0	4/5/85
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APPENDIX B - SAMPLE CALCULATION OF MINIMUM SAMPLE VOLUME

APPENDIX C - DIRECTIONS FOR DIOXIN SAMPLE SHIPMENT

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SECTION 1

PROJECT DESCRIPTION

Radian Corporation is under contract (EPA Contract Nos. 68-03-3148, Task 12 and 68-02-3850, Task 21) to the U. S. Environmental Protection Agency to conduct combustion source testing for Tier 4 of the National Dioxin* Study. As part of the Tier 4 effort, Radian will identify and conduct source tests at twelve (12) sites. The primary objective of the testing is to determine whether or not various combustion source categories emit 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), other dioxin isomers, and dibenzofuran isomers. For cases where the emission of dioxins or furans are found, a secondary objective will be to quantify these emissions and, if possible, to relate these emissions to combustion device operating conditions.

A parallel effort being conducted under Tier 4 involves the sampling and analysis of combustion device ash or control device particulate from approximately 50 sites. The results of these analyses will be used in conjunction with the source test results to determine if a relationship exists between the presence of dioxin/furan in combustion device ash and the presence of dioxin/furan in the flue gas.

The Tier 4 test program will be designed and executed with emphasis on completeness and data quality. A comprehensive quality assurance (QA) and quality control (QC) program will be an integral part of the overall test program. The goal of the QA/QC effort will be to ensure that the data collected are of known precision and accuracy and that they are complete, representative, and comparable.

A schedule of project activities and projected completion dates is presented in Figure 1-1.

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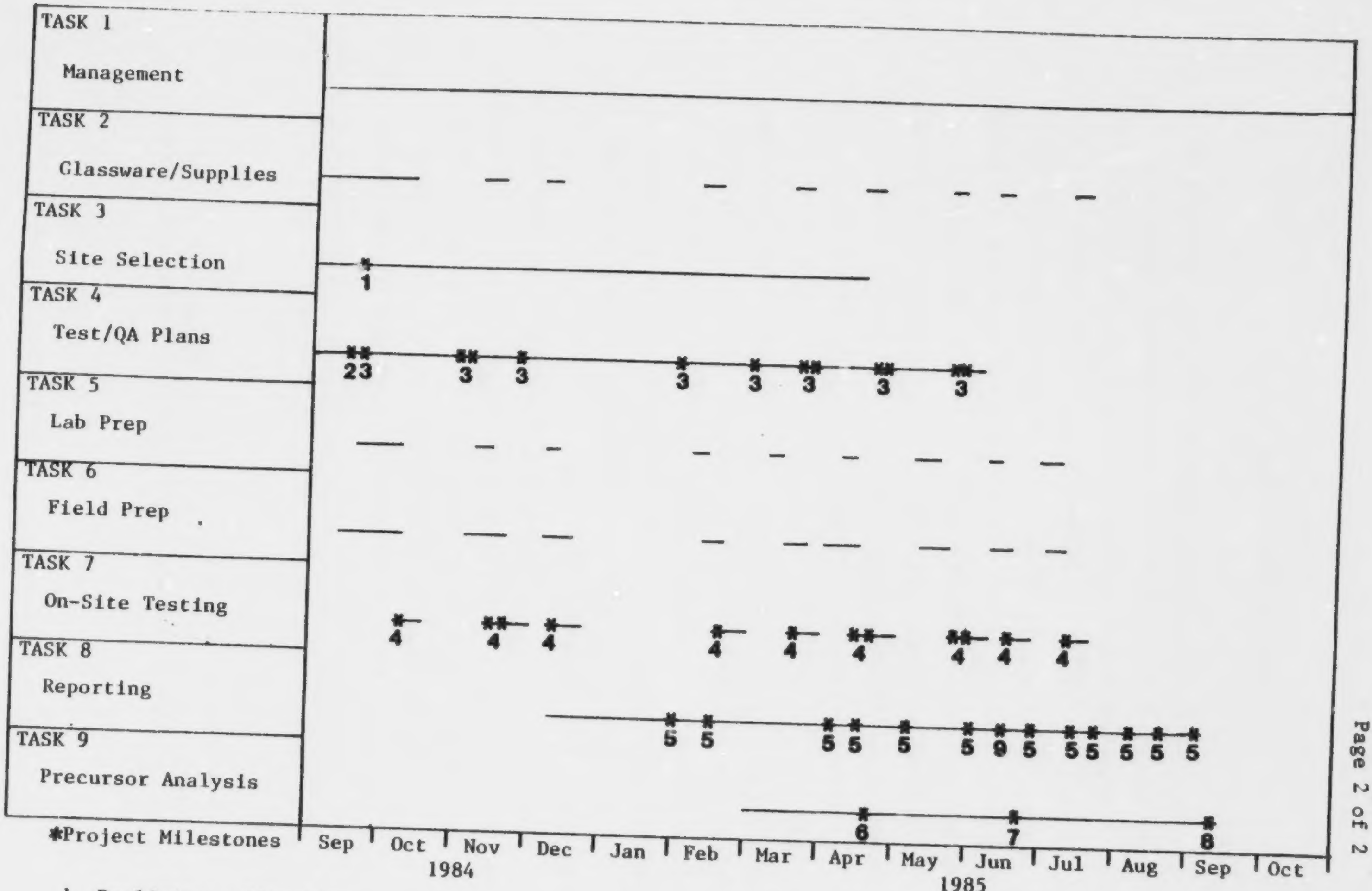
*Throughout this report, the term dioxin is used in the context of the report. Dioxin means 2,3,7,8-tetrachlorodibenzo-p-dioxin and the tetra- through octa-homologues.



1 Preliminary Site List
2 Draft QA Plan
3 Test Plans for Sites 1 to 12
4 On-Site Testing for Sites 1 to 12
5 Draft Test Reports for Sites 1 to 12
6 Precursor Results for Sites 1 to 5
7 Precursor Results for Sites 6 to 8
8 Precursor Results for Sites 9 to 12
9 Final Test Report for Site 1

FIGURE 1-1. SCHEDULE OF PROJECT ACTIVITIES THROUGH SEPTEMBER, 1985

SECTION 2

PROJECT ORGANIZATION AND RESPONSIBILITY

The project organization for the program is presented in Figure 2-1. The quality assurance (QA) and quality control (QC) functions have been organized to allow independent review of project activities while providing on-site QC coordination by the person most knowledgeable of the sampling/analysis activities.

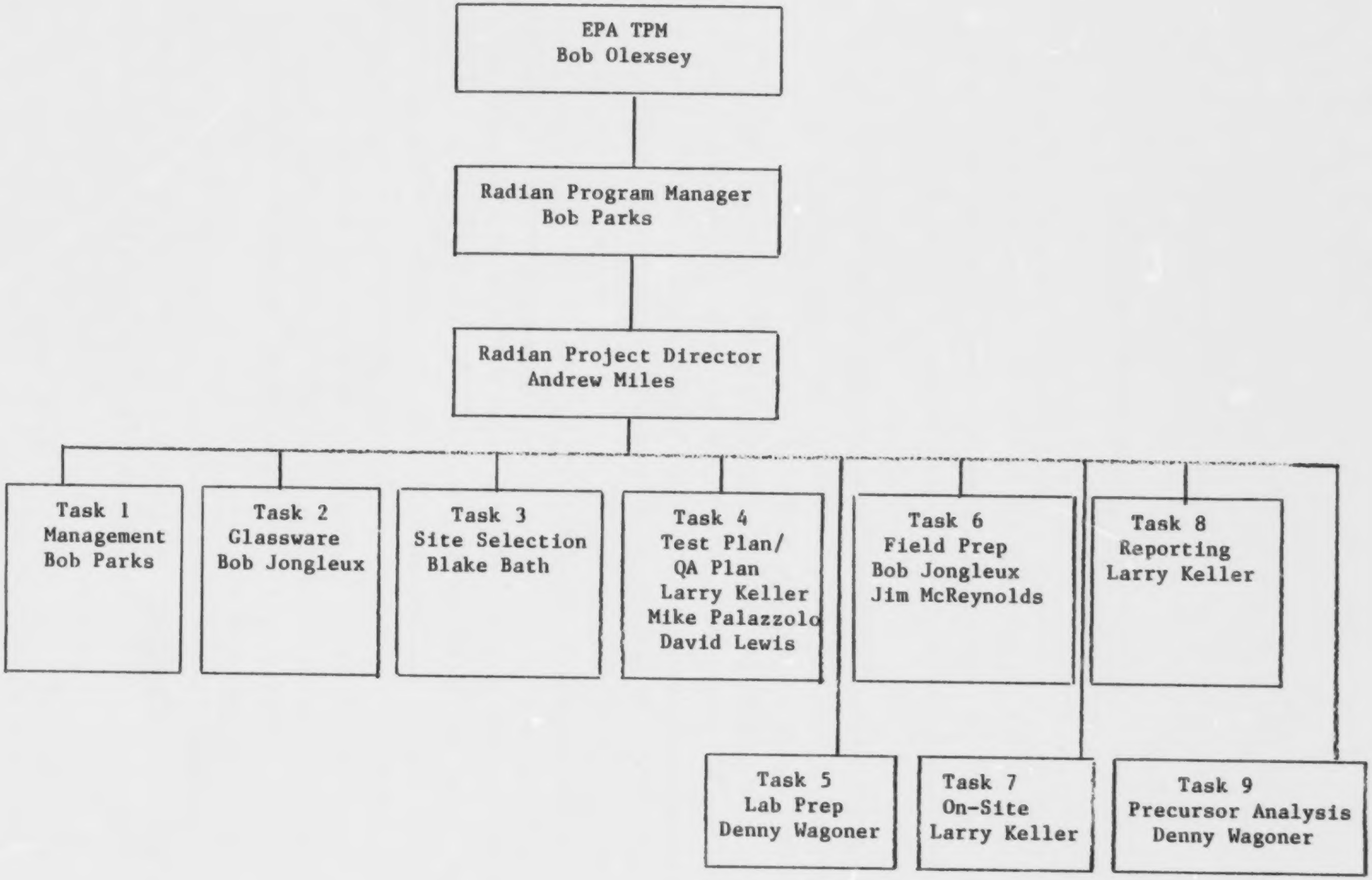
The objective of the quality control efforts for the program is to assess and document precision, accuracy, and adequacy of emission data developed during sampling and analysis.

The QA coordinator for this project is Mr. D. L. Lewis. He will coordinate the development and execution of the QA activities for the field testing effort. He is responsible for reviewing the QA Project Plan, evaluating the internal QC program, coordinating performance and systems audits, and documenting the results of all QA/QC activities.

As task leaders for the field testing task, Mr. M. A. Palazzolo and Mr. L. E. Keller will be responsible for implementing the project-specific system of quality control activities associated with the field testing effort. The Task Leader for laboratory preparation and precursor analysis, Mr. Denny Wagoner, will be responsible for implementing the project-specific quality control activities associated with the laboratory analytical effort.

The Project Director, Mr. Andrew J. Miles, is ultimately responsible for the overall technical effort. This includes responsibility for the timely, cost-effective execution of all project activities. He will also coordinate preparation of the final report.

This organization of QA/QC has proven to be effective in past Radian sampling/analysis programs. As problem areas and/or project priorities arise, the Field Task Leaders, who coordinate daily QC efforts, bring them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Management
Bob Parks
Task 2
Glassware
Bob Jongleux
Task 3
Site Selection
Blake Bath
Task 4
Test Plan/
QA Plan
Larry Keller
Mike Palazzolo
David Lewis
Task 6
Field Prep
Bob Jongleux
Jim McReynolds
Task 8
Reporting
Larry Keller
Task 5
Lab Prep
Denny Wagoner
Task 7
On-Site
Larry Keller
Task 9
Precursor Analysis
Denny Wagoner

Figure 2-1. Project organization chart.

to the attention of the Project Director for appropriate action. The QA coordinator provides independent review of QC activities and independent performance checks through QA audits.

SECTION 3.0

QUALITY ASSURANCE OBJECTIVES

The objective of the quality assurance efforts for this program is to assess and document the precision, accuracy and adequacy of the data collection systems including sampling and laboratory analysis. Table 3-1 summarizes the QA objectives for each of the major measurement parameters. Data comparability will be achieved by using standard units of measure as specified in the methods indicated in Table 3-1 and by using the same (or comparable) sampling and analytical methods at all test sites.

TABLE 3-1. SUMMARY OF ESTIMATED PRECISION, ACCURACY, AND DATA CAPTURE OBJECTIVES

Parameter	Precision	Accuracy	Data Capture[a]
Flue gas dioxins (modified Method 5)	To be determined by Troika		90%
Particulate mass (EPA Method 5)	11%[b]	±10%[b]	90%
HCl (acid train)	10%[e]	±7%[c]	90%
Velocity/volumetric flow rate (EPA Methods 1 and 2)	6%[b]	±10%[b]	95%
Fixed gases/molecular weight (modified EPA Method 3)	10%[d]	±20%[c]	90%
Moisture (EPA Method 4)	20%[b]	±10%[b]	90%
Flue gas O_2 (continuous monitor)	20%[d]	±20%[c]	90%
Flue gas CO (continuous monitor)	20%[d]	±20%[c]	90%
Flue gas CO_2 (continuous monitor)	20%[d]	±20%[c]	90%
Flue gas SO_2 (continuous monitor)	20%[d]	±20%[c]	90%
Flue gas NO_x (continuous monitor)	20%[d]	±20%[c]	90%
Flue gas THC (continuous monitor)	20%[d]	±25%[c]	90%
Chlorobenzenes (GC/MS)	50%[e]	±50%[f]	90%

Continued

TABLE 3-1. (CONTINUED)

Parameter	Precision	Accuracy	Data Capture[a]
Flue Chlorophenols (GC/MS)	50%[e]	±50%[f]	90%
Polychlorinated Biphenyls (GC/MS)	50%[e]	±50%[f]	90%
Total Chlorine	6%[e]	±30%[f]	90%

[a] Valid data percentage of total tests conducted.

[b] Precision and accuracy estimated based on results of EPA collaborative tests.

[c] Relative error (%) for audit analyses, where % =

$$\frac{\text{Measured Value} - \text{Actual Value}}{\text{Actual Value}} \times 100\%$$

[d] Coefficient of variation (CV) for daily analyses of control sample,

$$\text{where CV} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\%$$

[e] Percent difference for duplicate analyses, where % =

$$\frac{\text{First Value} - \text{Second Value}}{0.5\ (\text{First} + \text{Second Values})} \times 100\%$$

[f] Relative error (%) for GC/MS analysis based on spiked internal standards, where % =

$$\frac{\text{Measured Value} - \text{Spiked Value}}{\text{Spiked Value}} \times 100\%$$

SECTION 4

SAMPLING PROCEDURES

This section discusses the sampling methods which will be used to (1) obtain samples for dioxin analysis and (2) characterize the combustion source being sampled.

4.1 PRETEST SITE SURVEYS

As part of the site selection process, site surveys will be conducted prior to testing at each site. During the site survey, Radian personnel will obtain general plant information in addition to a detailed description of the facility and sampling locations. This information will be recorded on the pretest site survey form shown in Figure 4-1. Completion of this form will provide the information and establish the plant support necessary for timely and effective testing at each site.

4.2 GAS SAMPLING AND ANALYSIS METHODS

Manual and continuous gas sampling methods which will be used during this program are described in this section. These methods are summarized by sample location and measurement parameter in Table 4-1. As noted in Table 4-1, the measurement of certain parameters will not be necessary for all test sites. The need for these optional data will be determined on a site specific basis through consultation with the EPA Dioxin - Tier 4 Project Team. The parameters to be measured during each test will then be documented in the site specific test plan.

4.2.1 Manual Gas Sampling Procedures

Manual gas sampling methods will be used during this program to obtain (1) flue gas samples for dioxin and precursor analysis, (2) to determine particulate matter concentrations in the stack gases, and (3) to determine

GENERAL

Plant ____________________
Address ____________________
____
Phone ____________________ Date of Survey ____________________
Plant Personnel ____________________
Radian Personnel ____________________
Other Personnel ____________________
Primary Plant Contact ____________________
Phone (if different) ____________________

SITE DESCRIPTION

Type of process ____________________
____
____
Operating Schedule ____________________
____
____
Best Time to Test ____________________
Working Hours ____________________

FACILITY DESCRIPTION

Combustion Device ____________________
____
Manufacturer ____________________
Start-up Date ____________________
Operating Schedule ____________________
Capacity (lb steam/hr, Btu/hr, etc.) ____________________
Fuel
  What Fuels are Burned ____________________
  Fuel Source(s) ____________________
  Does Fuel Vary (how, how much, how often) ____________________
  ____
  ____
  Potential for Fuel Contamination with Precursors ____________________
  ____
  ____
Other Material Burned ____________________
____
____
____
Typical Operating Conditions (flows, temperatures,etc.) ____________________
____
____
____
Duty Cycle
  Are there variable operating conditions or feed materials ____________________
  If yes, what are they ____________________
  ____
  Is the feed containing the precursors continuous or
  or intermitant ____________________
Pollution Control Equipment Present ____________________
____
____
____

Figure 4-1. Pretest Site Survey Form

Description of Ash Handling System

Special Considerations, Operating History, Problems, Etc.

AVAILABLE PROCESS DATA
Access to Design Data
Access to O&M Logs
Can we get blank copies of operator logs
Data Available From the Plant Instrumentation
Combustion Device

Pollution Control Device

How often is data entered into the operating log

DRAWINGS

A separate page will be provided for each of the drawings listed below.

Elevation drawing of the facility with dimensions shown
Plot plan of the facility with dimensions shown
Plot plans for soil and pond sampling
Map (plot plan) showing surrounding industry
Sketches of sampling locations and hardware (as required)

FLOW DIAGRAMS

Flow diagram of combustion device and PCD showing sample locations
This should include, at a minimum, sample locations for fuel, waste feeds, ash, flue gas, quench water and scrubber blowdown.

SAMPLE POINT LOCATIONS AND DESCRIPTIONS
Sample Point Description (what is sampled, etc.)

Location
Process Stream
Type of Material (gas, liquid, slurry, sludge, solid)
Approximate % Water
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware

Figure 4-1. Pretest Site Survey Form (Continued)

____

____

Approximate Temperature and Pressure____________________

Sample Point Description (what is sampled, etc.)____________________

____

Location____________________
Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware____________________

____

____

Approximate Temperature and Pressure____________________

Sample Point Description (what is sampled, etc.)____________________

____

Location____________________
Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware____________________

____

____

Approximate Temperature and Pressure____________________

Sample Point Description (what is sampled, etc.)____________________

____

Location____________________
Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware____________________

____

____

Approximate Temperature and Pressure____________________

Sample Point Description (what is sampled, etc.)____________________

____

Location____________________

Figure 4-1. Pretest Site Survey Form (Continued)

Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing)
and what is the size of the hardware____________________
____
____
____
Approximate Temperature and Pressure____________________

Sample Point Description (what is sampled, etc.)____________________
____
____
Location____________________
Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing)
and what is the size of the hardware____________________
____
____
____
Approximate Temperature and Pressure____________________

Sample Point Description (what is sampled, etc.)____________________
____
____
Location____________________
Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing)
and what is the size of the hardware____________________
____
____
____
Approximate Temperature and Pressure____________________

Sample Point Description (what is sampled, etc.)____________________
____
____
Location____________________
Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing)
and what is the size of the hardware____________________
____
____
____
Approximate Temperature and Pressure____________________

Figure 4-1. Pretest Site Survey Form (Continued)

SAMPLING CONSIDERATIONS

Are fuel samples available____________________

How can they be taken____________________

Are ash samples available____________________

How can they be taken____________________

Length(s) of heat traced sample line necessary (show on diagrams)____

Sampling Locations Requiring Special Access____________________

Will Plant Provide This Special Access____________________

Other____________________

MOBILE LAB AND OTHER SUPPORT FACILITIES

Space Available (where, how much, show on plot plan drawing)________

Available Utilities

Electrical (voltage, amperage, phase for each circuit)________

Other____________________

Generator operation OK?____________________

Area for temporary equipment and sample storage____________________

Other Support Facilities

Phone available____________________Number____________________

Access to Copier____________________

Access to Office Space____________________

SPECIAL REQIREMENTS AND SITUATIONS

Scaffolding Requirements____________________

Other Special Access Requirements____________________

Special Safety Requirements____________________

What is required to obtain access to plant (letters, agreements, etc

Confidentially Issues____________________

Other____________________

Figure 4-1. Pretest Site Survey Form (Continued)

TABLE 4-1. SUMMARY OF GAS SAMPLING METHODS

Sample Location	Sample Type or Parameter	Sample Collection Method
Combustion Device Outlet	Dioxin/furan	Modified EPA Method 5
	Volumetric Flow	EPA Method 2
	Molecular Weight	EPA Method 3
	Moisture	EPA Method 4
	CO	Continuous Monitor
	CO_2	Continuous Monitor
	O_2	Continuous Monitor
	NO_x[b]	Continuous Monitor
	SO_x[b]	Continuous Monitor
	THC	Continuous Monitor
Stack Exhaust	Dioxin/furan	Modified EPA Method 5
	Particulate[b]	EPA Method 5
	Volumetric Flow	EPA Method 2
	Molecular Weight	EPA Method 3
	Moisture	EPA Method 4
	HCl[b]	Acid Train
Combustion Air	Dioxin/furan	Ambient XAD Train[c]
	Precursors	Ambient XAD Train[c]

[a] Polychlorinated dibenzo-p-dioxin and dibenzofuran homologues with 3 to 8 chlorines and 2,3,7,8-TCDD.

[b] Optional.

[c] Ambient air sample train using XAD-2 resin for trapping organic constituents (see (Section 4.2.1).

HCl concentrations in the stack gases. Manual methods will also be used to measure gas velocity/volumetric flow and moisture content and to obtain samples for molecular weight determinations. These methods are discussed in the sections below.

4.2.1.2 Flue Gas Dioxin/Furan Determination. Gas sampling for dioxin/furan will be conducted according to the latest draft of the ASME chlorinated organic compound sampling protocol with several modifications. The draft ASME protocol is attached to this QAPP as Appendix A. Necessary changes to the protocol that have or will be implemented for the Tier 4 source tests are discussed in the appropriate sections below.

The ASME sampling method is a modified version of EPA Method 5 that includes a solid sorbent module for trapping vapor phase organics. The Modified Method 5 (MM5) sampling train will be used to collect samples at the combustion device outlet and emission control device exhaust stack. Following sample recovery, the various parts of the sample (filter, solvent rinses, sorbent trap, etc.) will be sent to the EPA's Troika laboratories to quantify the 2,3,7,8-TCDD and tetra- through octa-dioxin and furan homologues present in the samples.

A total of three MM5 test runs will be conducted at each sampling location with one test run being conducted per test day. The MM5 sample will be collected isokinetically over a 3-hour sampling period at the combustion device outlet and a 4-hour period at the system exhaust stack. The sampling rate at both locations will be between 0.5 and 0.75 scfm to provide minimum sample volumes of 90 scf at the combustion device outlet and 120 scf at the exhaust stack. This sample should allow detection of 1 part per trillion (ppt) of 2,3,7,8-TCDD in the stack gas at the minimum detection limit for Troika's analysis. The calculation for the minimum sample time required is attached as Appendix B.

Sampling Train Description

A schematic diagram of the MM5 sampling train is shown in Figure 4-2. Flue gas is pulled from the stack through a nozzle and heated glass probe. Particulate matter is removed from the gas stream by means of a glass fiber filter housed in a teflon-sealed glass filter holder maintained at 248 ±

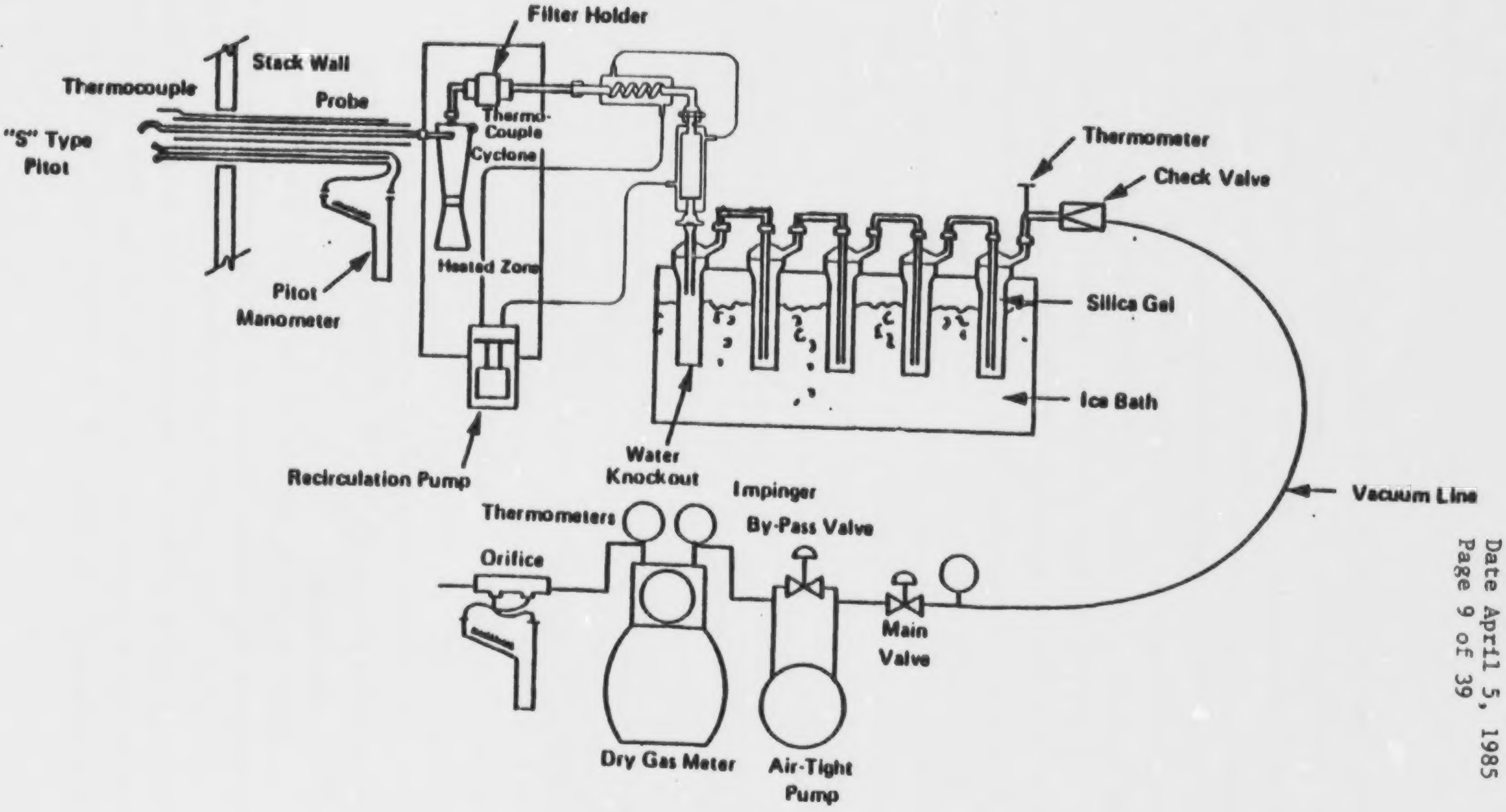

Filter Holder
Stack Wall
Thermocouple
Probe
"S" Type Pitot
Thermo-Couple
Cyclone
Thermometer
Check Valve
Heated Zone
Silica Gel
Pitot Manometer
Ice Bath
Recirculation Pump
Water Knockout
Vacuum Line
Impinger
Thermometers
By-Pass Valve
Orifice
Main Valve
Dry Gas Meter
Air-Tight Pump

Figure 4-2. Modified Method 5 Train

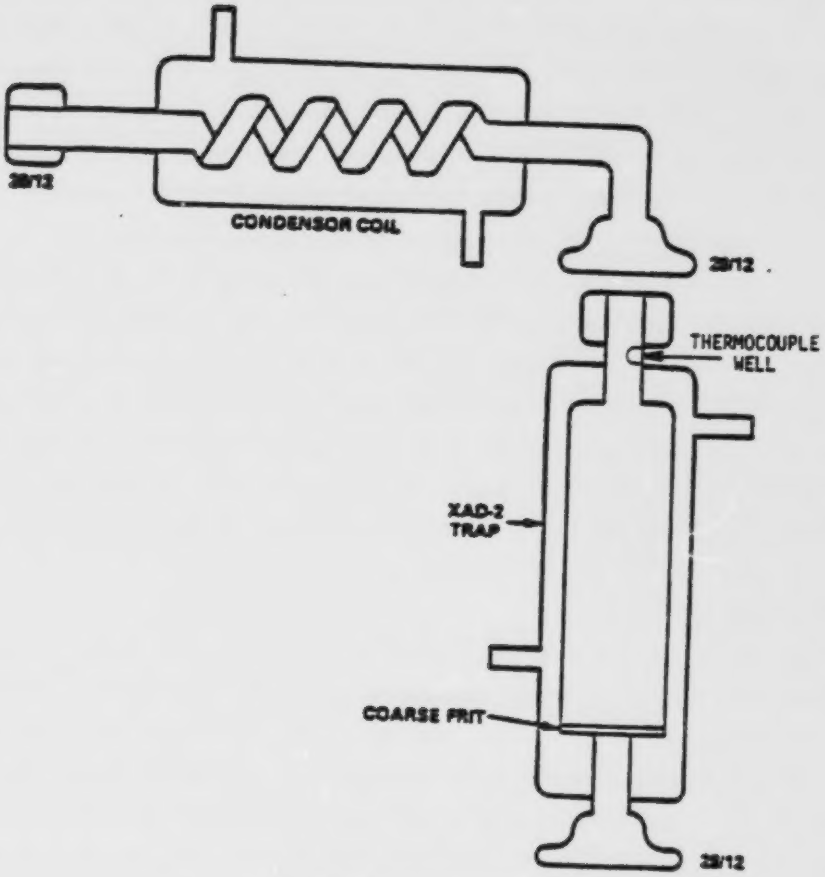
25°F. The filter holder contains a teflon coated stainless steel frit to support the filter. The gas passes through a sorbent trap for removal of organic constituents. The trap, which is illustrated in Figure 4-3, consists of separate sections for (1) cooling the gas stream, and (2) adsorbing the organic compounds on Amberlite XAD-2® resin (XAD). A chilled impinger train is used to remove water from the flue gas and a dry gas meter is used to measure the sample gas flow.

The ASME protocol stipulates that both the condenser coil and the resin trap be oriented vertically. Radian has found, however, that substitution of a horizontal condenser coil (but not trap) works equally well without causing significant holdup of condensate in the coil or channeling of the condensate through the resin. The horizontal coil has an additional advantage of reducing the space required for traversing the sampling train. Throughout the Tier 4 dioxin testing a horizontal condenser coil with a vertical resin trap will be used.

Other modifications to the MM5 sample train described above may be necessary depending on the particular combustion sources or sampling locations tested during this program. For conditions where particulate loadings are exceptionally high, a cyclone will be used upstream of the filter to reduce the need for frequent filter changes. In cases where flue gas moisture contents are exceptionally high, the first modified Greenburg-Smith impinger in the MM5 sample train will be replaced by an oversize impinger to prevent the need to disassemble the train and empty the impingers prior to completing the test run. Any necessary modifications of this type will be documented in the site-specific test plans, which should be approved by the EPA Project Officer prior to testing.

Filter Preparation

Prior to use in the field, the glass fiber (RA934AH) filters will be precleaned and checked for contamination. A total of 50 filters from the same lot will be extracted simultaneously with hexane in a Soxhlet extractor for a period of 24 hours. The extract will be analyzed first by Radian on a varian gas chromatography to verify that the filters are free of contamination. An aliquot of the extract will then be sent to Troika for


28/12
CONDENSOR COIL
28/12
THERMOCOUPLE WELL
XAD-2 TRAP
COARSE FRIT
28/12

XAD-2 Trap and Condenser Coil.

Figure 4-3. Adsorbent Sampling System

analysis for dioxin. The precleaned filters will be used in the field for sample collection. To prevent contamination of the filters, the filters will be placed in a precleaned petri dish and sealed with teflon tape.

XAD Preparation

Cleanup of the XAD-2 resin will be conducted according to the procedures outlined in the ASME protocol with one modification. For the first three dioxin source tests, hexane was used as the final solvent for preparation of the resin as specified in the protocol. However, use of hexane as the final solvent was shown to cause interference with the analysis for dioxin. For all tests conducted after Site 03, benzene will be substituted for hexane as the final resin preparation solvent.

All other procedures for XAD preparation have and will be conducted according to the ASME protocol. The fluidized bed technique will be used to dry the resin. Care will be taken to ensure that the resin is kept at temperatures below 120°F before and after sample collection to prevent resin decomposition. The sorbent tube will be charged with 20 to 30 grams of the precleaned resin. The period of time between resin precleaning and use in the field will be minimized and will not be allowed to exceed 6-weeks.

Glassware Preparation

All glass parts of the MM5 sample train including the sorbent tube, will be precleaned prior to sampling according to the procedure listed in Table 4-2. The purpose for substituting methylene chloride for hexane in the glassware cleaning procedure after Site 03 is discussed below under "Sample Recovery." Cleaned glassware will be capped with precleaned foil or glass plugs until sample train assembly in the field. Following sample recovery, the glassware may be reused at the same sampling location. Sealing greases will not be used on the sample train.

Sample Train Operation

The sample train will be operated according to the ASME Protocol. Special attention will be given to the following QC checks:

TABLE 4-2. GLASSWARE PRECLEANING PROCEDURE

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

1. Soak all glassware in hot soapy water (Alconox^R) 50°C or higher.
2. H_2O rinse (X3)[a].
3. Distilled/deionized H_2O rinse (X3).
4. Chromerge^R rinse if glass, otherwise skip to 6.
5. High purity liquid chromatography grade H_2O rinse (X3).
6. Acetone rinse (X3), (pesticide grade).
7. Methylene chloride[b] rinse (X3), (pesticide grade).
8. Oven dry (110°C - 2 hrs).
9. Cap glassware with clean glass plugs or $MeCl_2$ rinsed aluminum foil.

---

[a] (X3) = three times.
[b] For Sites 01 through 04 hexane was used as the solvent for this last rinse.

1. The entire sample train will be leak tested to ensure that leakage does not exceed the lesser of (a) 4 percent of the average sampling rate, or (b) 0.02 cfm.

2. Leak checks will be conducted before and after each run. If the sampling train is moved from one sampling port to another during a run, the train will be leak checked before and after the move.

4. The probe temperature will be maintained above 248°F, and the filter holder will be maintained at 248 ± 25°F during sampling.

4. Gas entering the sorbent module will be maintained at or below 68°F.

5. Isokinetic sampling will be maintained within ±10 percent.

If a sample train leak is found after testing has begun, the following procedure will be implemented:

1. The field team leader will be immediately notified of the problem.

2. The location and quantity of the leak in the sample train will be identified.

3. Based on the location and quantity of the leak, the portion of the sampling run completed at the time of the leak and the projected impact of the problem on the particular sample and the overall test effort, the team leader will decide whether to abort or continue the test run.

4. All occurrences of sample train leaks and the corrective action taken will be noted on the data sheet and documented in the daily logbook discussed in Section 6.

Sample Recovery

Recovery of the MM5 samples and assembly of the sample trains will be conducted in an environment free from uncontrolled dust, such as a vehicle or lab; access to this area will be limited to only those individuals involved in the recovery process.

The sample containers from a typical MM5 test run will include those shown in Table 4-3. All dioxin sample containers containing water should be extracted for analysis by Troika within 7 to 14 days after sample collection. It should be noted that depending on the particulate loading and/or the flue gas moisture content, the actual number of containers from

TABLE 4-3. TYPICAL MODIFIED METHOD 5 SAMPLING, TRAIN COMPONENTS OR CONTAINERS TO BE SHIPPED TO TROIKA.

Container/Component	Contents
1. Container Number 1 or Filter Holder[a]	Filter(s)
2. Container (inlet only)[b]	Cyclone catch, if used
3. Container Number 2	Rinses[c] of nozzle, probe, transfer line, cyclone, and front half of filter holder
4. Sorbent Module	XAD-2® resin
5. Container Number 3	Rinses of back half of filter holder, condenser rinse, water knockout trap (optional)
6. Container Number 4	First impinger contents and rinse

[a] Filter and filter holder may be shipped capped.

[b] Not needed for outlet of control device.

[c] Rinses include acetone and methylene chloride combined in same container.

each sample run will vary. The need for three or more filters (and corresponding additional solvent rinses) is not unusual for gas streams with high particulate loadings. Also, a significant quantity of water may be collected from high moisture content gas streams.

Solvents used for rinsing the nozzle, probe, filter holder and cyclone (if used) have been modified several times during the period that the first five dioxin source tests were conducted. For Site 01 recovery of the glassware involved rinsing with deionized (DI) water, acetone, and then hexane three times each. This procedure was changed for Sites 02 and 03 to eliminate the water rinse due to a revision of the ASME protocol (April 16, 1984 version versus October, 1984 version). Water was again reinstituted as the first of three solvents for Sites 04 and 05, both of which were black liquor recovery boilers. The use of water for these particular sources is necessary to ensure recovery of acetone insoluble particulate from the glassware.

The latest change in the glassware rinsing scheme was the substitution of methylene chloride for hexane to improve recovery of dioxin present in the sample. This change will be implemented for all test sites beginning with Site 05.

Sample Train Blanks

A single field blank will be obtained for each MM5 sampling location. Three portions of a sample train (impingers/sorbent trap, filter holder, and probe) will be assembled at the location as though to collect a sample, but no gas will be pulled through the train. The train will be disassembled (into three portions) and returned to the mobile laboratory for recovery using the same procedure used to recover actual samples. The field blank will be obtained using a train that has previously been used to collect at least one actual sample from the test site.

An MM5 "proof" blank will also be obtained for each Tier 4 source test beginning with Site 05. The proof blank will be obtained from a complete set of MM5 sample train glassware that has been cleaned according to the procedure presented in Table 4-2. The pre-cleaned glassware, which consists of a probe liner, filter holder, condenser coil and impinger set, will be rinsed with acetone and methylene chloride three times each. Analysis of the rinse will be used to check the effectiveness of the glassware cleaning procedure. Blanks of the solvents used at each test site will also be saved for potential future analysis.

4.2.1.3 Combustion Air Dioxin and Precursors Determination

At test sites located in areas with potential for significant levels (ppmv) of precursors or dioxins to be present, collection of precombustion (ambient) air samples may be desirable for total TCDD and precursor analysis. Such sites include combustion devices located adjacent to and downwind of (1) chemical facilities producing or using chlorinated organics, (2) poorly controlled combustion sources, or (3) wood treatment facilities Organic compounds in the ambient air will be collected on an XAD sorbent trap using a sample train similar to that used for Modified Method 5.

A schematic diagram of the "ambient XAD" sample train is shown in Figure 4-4. The ambient train consists of a short glass probe, sorbent tube, knockout impinger (optional), silica gel impinger, umbilical line, pump, and dry gas meter. Ambient air will be drawn into the sorbent module, where it will be cooled to 68°F or lower, and the organic constituents will be adsorbed by the XAD resin. The gas will then be dried with the silica gel and the sample volume measured by the dry gas meter. Two separate sample trains will be run simultaneously. One of the XAD tubes will be analyzed by Troika for total TCDD, and the other tube will be analyzed for dioxin precursors at Radian's RTP laboratory. Analytical procedures for the precursor analysis are discussed in Section 5.0.

The entire ambient XAD sample train will be leak tested before and after each test run at 10 inches H_2O to ensure that the total leakage is less than 0.02 cfm. The ambient XAD sample train will be operated during the same time periods that the MM5 samples are being collected, but the XAD trap will be kept cold (68°F or lower) 24 hours per day. The same set of XAD traps will be used during all three MM5 test runs, thus providing composite combustion air samples for each site. The dry gas meter reading will be recorded twice daily at the beginning and end of each test period.

AMBIENT XAD TRAIN

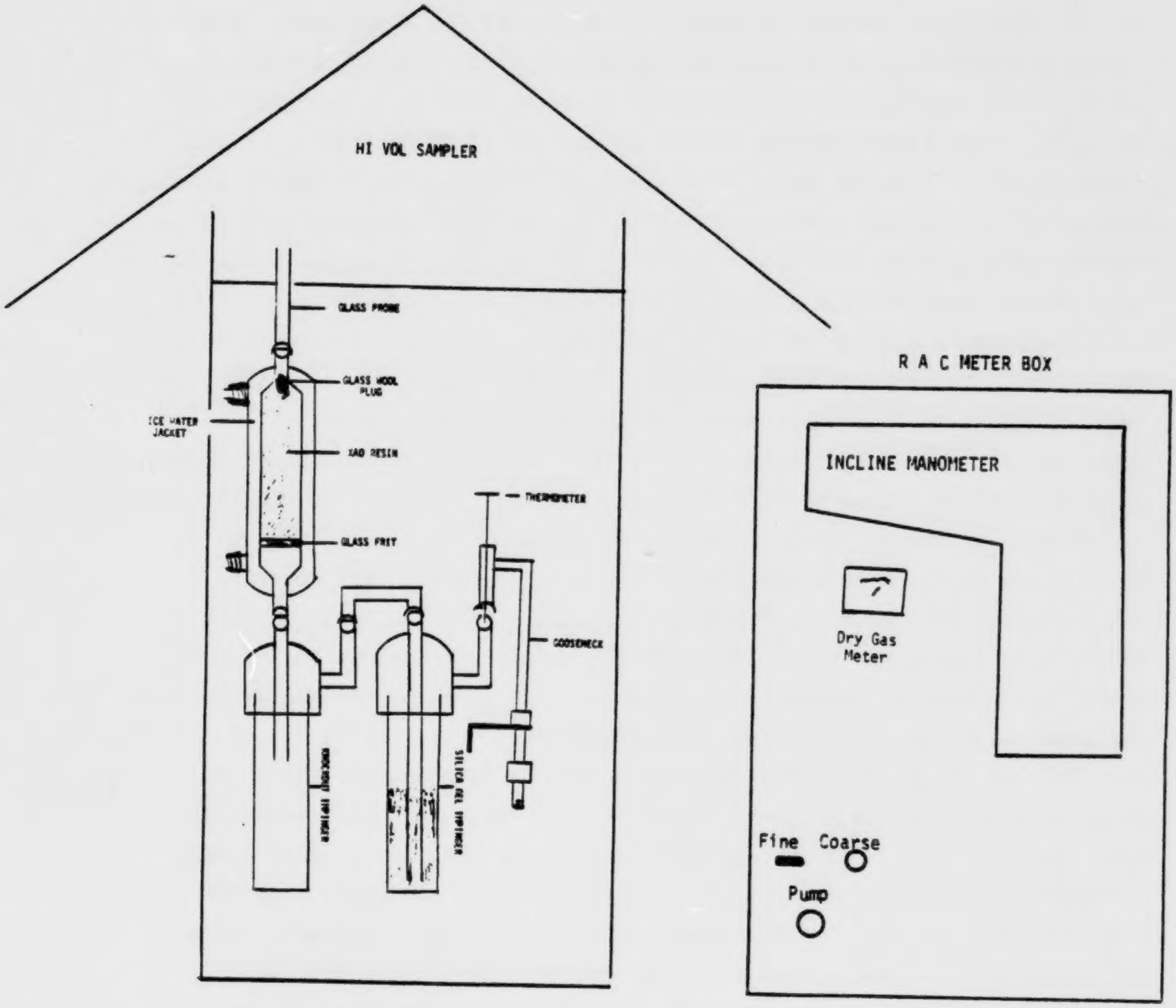

HI VOL SAMPLER
GLASS PROBE
GLASS WOOL PLUG
ICE WATER JACKET
XAD RESIN
THERMOMETER
GLASS FRIT
GOOSENECK
KNOCKOUT IMPINGER
SILICA GEL IMPINGER
R A C METER BOX
INCLINE MANOMETER
Dry Gas Meter
Fine
Coarse
Pump

Figure 4-4. Diagram of Ambient XAD Train

The dry gas meter temperature, ice bath temperatures, pressure, and volume will be recorded once per hour during the sampling periods.

Recovery of the ambient XAD sample train will be performed in a manner similar to that of the MM5 train. The probe will be rinsed with acetone and methylene chloride three times each, and this rinse will be stored in a single sample container. The sorbent tube will be capped with ground glass caps. If the optional knockout impinger is used, the impinger will be rinsed with acetone and methylene chloride, and the condensate and rinse will be combined in a single container. The optional knockout will only be needed for very hot, humid ambient air sampling.

4.2.1.4 Particulate Grain Loading Determinations

The sampling procedures specified in EPA Method 5 will be used to determine the total particulate grain loading during this program (1). Particulate loadings will not be determined at all test sites, but only in those cases where these data are considered desirable by the EPA/Radian Tier 4 project team.

A schematic diagram of EPA Method 5 sampling train is shown in Figure 4-5. Based on this method, a sample of the particulate-laden flue gas is extracted isokinetically from the stack using a stainless steel buttonhook nozzle and glass-lined probe. The particulate matter is removed from the gas by means of an out-of-stack glass fiber filter. A chilled impinger train is used to remove water from the flue gas. A pump and dry gas meter are used to control and monitor the glass flow rate.

4.2.1.5 HCl Determination

HCl concentrations in the flue gas will be determined using another modification of EPA Method 5. As with the particulate loadings, HCl emissions will not be determined at all test sites. The sample train components and operations are identical to those of Method 5 with the following exceptions:

1. Water in the first two impingers will be replaced with either 0.1m NaOH or KOH.

2. The sampling will be single point isokinetic with the nozzle placed at a point in the stack of average velocity.

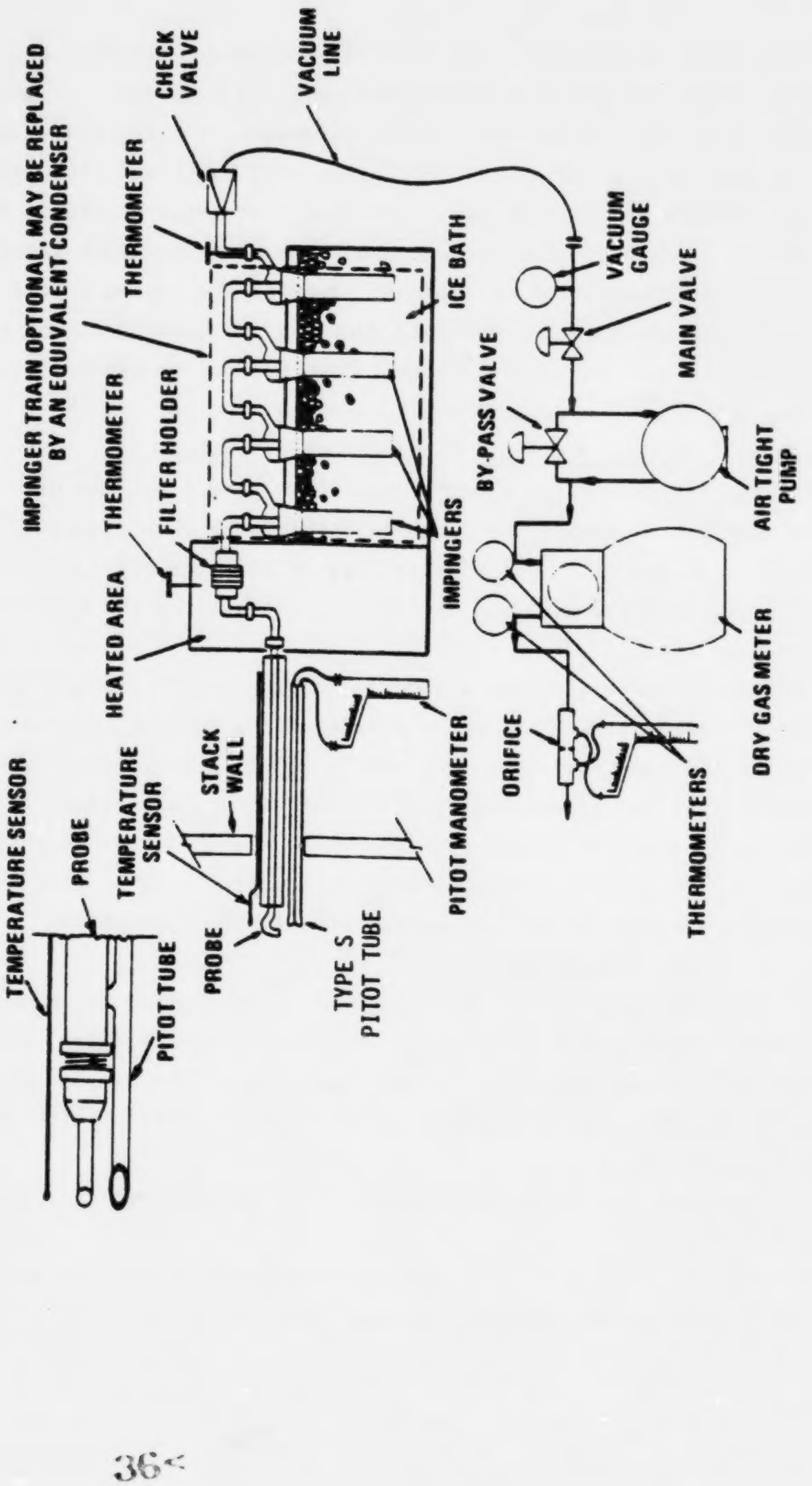

TEMPERATURE SENSOR
PROBE
PITOT TUBE
TEMPERATURE SENSOR
PROBE
TYPE S PITOT TUBE
STACK WALL
PITOT MANOMETER
HEATED AREA
THERMOMETER
FILTER HOLDER
IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSER
IMPINGERS
THERMOMETER
ICE BATH
CHECK VALVE
VACUUM LINE
VACUUM GAUGE
MAIN VALVE
BY-PASS VALVE
AIR TIGHT PUMP
DRY GAS METER
ORIFICE
THERMOMETERS
THERMOMETERS

Figure 4-5. Schematic of Method 5 Sampling Train

3. The recovered moisture and the NaOH or KOH in the impingers will be saved for laboratory analysis by ion chromatography. The impinger catch will be stored at 4°C until analysis.

4.1.2.6 Volumetric Gas Flow Rate Determination

The volumetric gas flow rate will be determined during this program using procedures described in EPA Method 2 (2). Based on this method, the volumetric gas flow rate is determine by measuring the cross-sectional area of the duct and the average velocity of the flue gas.

The average flue gas velocity is calculated from the average gas velocity pressure (ΔP), the average flue gas temperature, wet molecular weight, and the absolute static pressure. ΔP and temperature profile data will be obtained by traversing the duct. The number of sampling points required to measure the average gas velocity will be determined using the procedures outlined in EPA Method 1 (2). The number of sampling points and their distance from the duct wall is a function of the proximity of the sampling location to its nearest upstream and downstream flow disturbance.

ΔP and temperature profile data will be measured at each of the sampling points using an S-type pitot tube and K-type thermocouple. An inclined oil monometer of the proper range will be used to measure the pressure drop (Δ) across the S-type pitot. A mercury or calibrated aneroid barometer will be used to obtain barometric pressure readings at least twice a day. The static gas pressure at the scrubber inlet and outlet will be measured by disconnecting one side of the S-type pitot and then rotating the pitot so that it is perpendicular to the gas flow. A Magnehelic® gauge will be attached to the S-type pitot to measure the static pressure within the duct.

4.2.1.7 Flue Gas Moisture Determination

The moisture content of the flue gas will be determined using the methodology described in EPA Method 4 (3). Based on this method, a known volume of particulate-free gas is pulled through a chilled impinger train. The quantity of condensed water is determined gravimetrically and then related to the volume of gas sampled to determine the moisture content. During this project, the moisture content of the flue gas will be determined during the operation of the MM5, Method 5, and HCl sampling trains. The impingers used with these sampling trains will be weighed before and after sampling. The mass increase (H_2O) will then be related to the volume of gas sampled to calculate the moisture content.

4.1.2.8 Flue Gas Molecular Weight Determination

During testing, the integrated sampling technique described in EPA Method 3 (4) will be used to obtain a composite flue gas sample for fixed gas (O_2, CO_2, N_2) analysis. A small diaphram pump and a stainless steel probe will be used to extract a single point flue gas sample which will be collected in a Tedlar® bag. Moisture will be removed from the gas sample by a water-cooled condenser so that the fixed gas analysis is on a dry basis.

The composition of the gas sample will be determined using a Shimadzu Model 3BT analyzer as opposed to the Fyrite or Orsat analyzer prescribed in Method 3. This instrument employs a 1 ml sample loop, dual gas chromatographic columns, and dual thermal conductivity detectors (TCD). When the gas sample is introduced from the loop, it is first carried into Column 1. This column holds up CO_2 while the rest of the sample passes quickly through the column to the first TC detector producing a composite peak. The CO_2 is then eluted from Column 1 and detected by the first TC detector. This peak is used for CO_2 quantitation. The early eluting composite and the CO_2 fraction is permanently adsorbed while the remaining portion of the original sample is chromatographically separated into its components. These separated components elute from Column 2 to be individually detected by the second TC detector. The operating parameters for the analysis are:

- Column 1: 1/8" x 4.5' stainless steel packed with Chromosorb 102®,
- Column 2: 1/8" x 15' stainless steel packed with Molecular Sieve 5A^R,
- Oven temperature: 30°C, and
- Carrier gas: He at 1.6 kP/cm^2 at regulator No. 2.

4.2.2 Continuous Gas Sampling/Analysis Procedures

Continuous monitoring for a number of flue gas parameters will be conducted during this program to characterize the operation of the combustion device. Whenever possible, these parameters will be monitored at the combustion device outlet, prior to any emission control equipment. Otherwise, the flue gas parameters will be monitored at the control equipment exhaust stack. Continuous monitoring for CO, CO_2, O_2, and total hydrocarbons (THC) will be performed at all test sites. NO_x and SO_2 will be monitored only at those sites where these data are considered desirable by the EPA/Radian Project Team.

The continuous monitoring will be performed throughout the 4 to 6-hour period that dioxin sampling is being conducted each test day. The primary intent of the continuous monitoring effort is to (1) observe fluctuations in flue gas parameters and (2) provide an indication of combustion conditions. While the continuous monitors will be calibrated daily according to the procedures outlined in Section 7.0 of this QA Project Plan, no attempt will be made to certify the monitors or monitoring locations through relative accuracy tests with the EPA reference methods.

The sampling and analytical systems which will be used to determine CO, CO_2, O_2, THC, NO_x and SO_2 are discussed below.

4.2.2.1 Sample Acquisition. Sample acquisition will be accomplished using an in-stack filter probe and a heat-traced Teflon® umbilical connected to a mobile laboratory as shown in Figure 4-6. The heat-traced umbilical will be maintained at a temperature of at least 120°C to prevent condensation in the sample line. The stack gas sample will be drawn through the filter and umbilical using pumps located in or near the mobile laboratory. Sample gas to be analyzed for CO, CO_2, O_2, NO_x and SO_2 will be pumped through a sample gas conditioner, consisting of an ice bath and knockout trap, to remove moisture and thus provide a dry gas stream for analysis. A separate unconditioned heated gas slip stream will be supplied to the THC analyzer for analysis on a wet basis. Sample gas from the gas conditioner will be pumped into a glass or stainless steel sample manifold at a flow rate which exceeds the total sample requirements of the various gas monitors. The sampling manifold will thus be used to provide slip stream sample flows to each monitor.

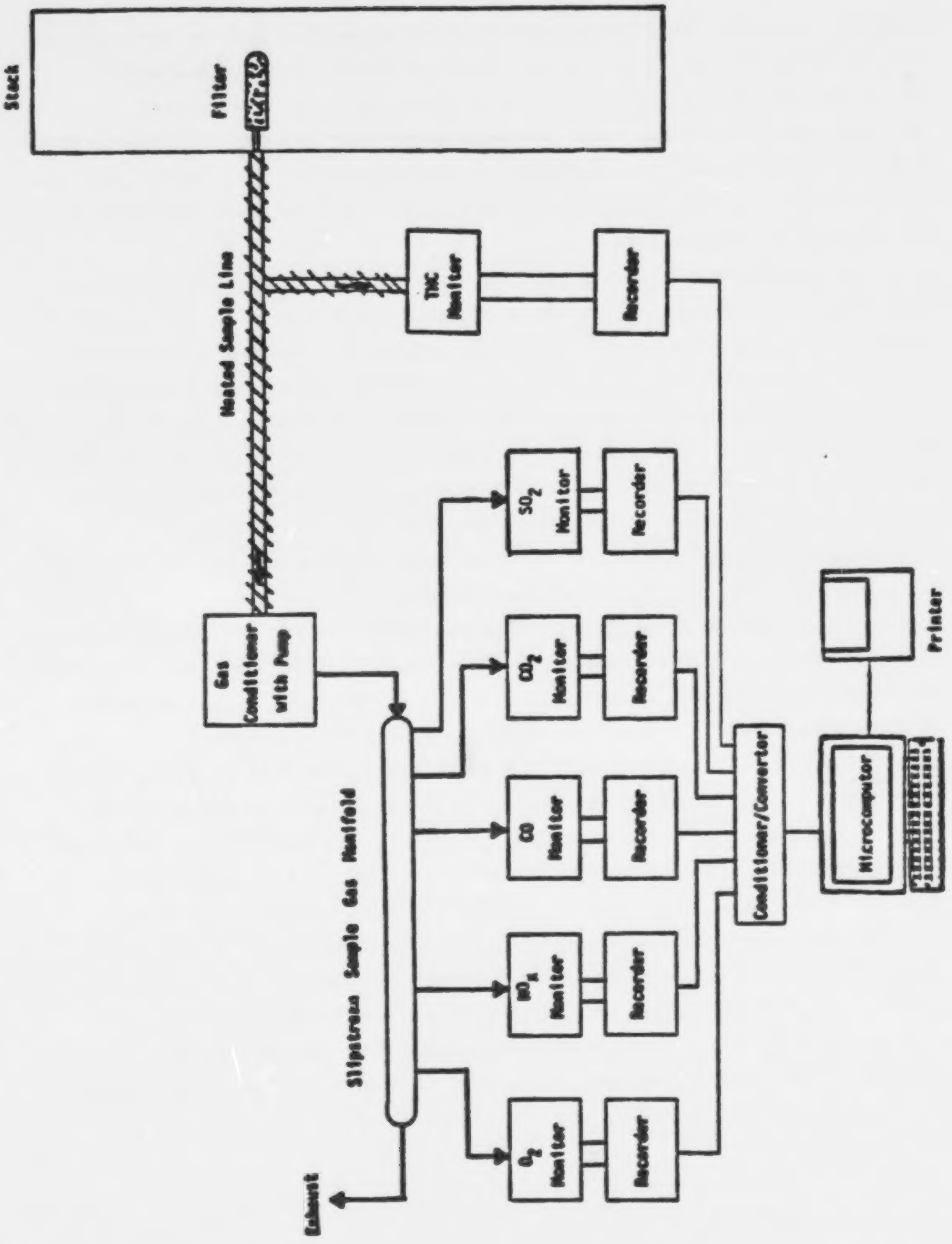

Stack
Filter
Heated Sample Line
THC Monitor
Recorder
Gas Conditioner with Pump
SO_2 Monitor
Recorder
CO_2 Monitor
Recorder
CO Monitor
Recorder
NO_x Monitor
Recorder
O_2 Monitor
Recorder
Slipstream Sample Gas Manifold
Exhaust
Conditioner/Converter
Microcomputer
Printer

Figure 4-6. Continuous Monitor Sample Acquisition System

To ensure representative measurements, all gases for calibration (except those for the THC analyzer) will be introduced at the inlet of the gas sample conditioner. The THC calibration gases will be introduced directly into the instrument. The heat-traced umbilical will be cleaned with acetone (if necessary) prior to each test and will be blanked for hydrocarbons and tested for air inleakage prior to the start of testing at each site. This system blank and leak check will be accomplished by disconnecting the filter probe and introducing zero nitrogen at the inlet of the heat-traced umbilical.

4.2.2.2 Carbon Monoxide/Carbon Dioxide Analysis. An Anarad Model 412 analyzer will be used to measure CO and CO_2 concentrations in the flue gas. The Anarad 412 is a non-dispersive infrared (NDIR) analyzer. The instrument measures the concentration of CO and CO_2 by infrared absorption at a characteristic wave length.

4.2.2.3 Oxygen Analysis. A Beckman 755 Oxygen Analyzer will be used to determine oxygen concentrations. The Beckman 755 measures O_2 concentrations on the basis of the strong paramagnetic properties of O_2 compared to other compounds present in combustion gases. In the presence of a strong magnetic field, O_2 molecules become temporary magnets. The Beckman 755 determines the sample gas O_2 concentration by detecting the displacement torque of the sample gas on a test body in the presence of a magnetic field.

4.2.2.4 Total Hydrocarbon Analysis. A Beckman Model 402 hydrocarbon analyzer will be used to measure total hydrocarbons (THC) in the flue gas. This instrument is a continuous flame ionization analyzer (FIA). The detector is a burner where a regulated flow of sample gas passes through a flame sustained by regulated amounts of air and hydrogen. Hydrocarbons passing through the flame undergo a complex ionization that produces electrons that are detected by polarized electrodes. The THC analyzer will be calibrated using propane standards, and sample concentrations will be reported as parts per million by volume (ppmv) as propane.

4.2.2.5 Nitrogen Oxides (NO_x) Analysis. A Teco Model 10AR analyzer will be used for NO_x measurement. This instrument determines NO_x concentrations by converting all nitrogen oxides present in the sample to nitric oxide and then reacting the nitric oxide with ozone. The reaction produces a chemiluminescence proportional to the NO_X concentration in the sample. The chemiluminescence is measured using a high-sensitivity photomultiplier.

4.2.2.6 Sulfur Dioxide Analysis. Sulfur dioxide in the flue gas will be measured using a Teco Model 40 pulsed fluorescent analyzer. This instrument measures SO_2 concentration on the basis of the fluorescence of SO_2 produced by its absorption of ultraviolet radiation. An important consideration for this method of SO_2 measurement is the potential for quenching of the instrument response by flue gas components such as CO_2 and O_2. If the concentrations of CO_2 and O_2 in the sample gas are different from those in the calibration gas, the SO_2 response for the sample will be corrected for this quenching effect. Calculations required for this correction are presented in Section 7.0. These corrections will be made based on flue gas CO_2 and O_2 measurements made with Anarad 412 and Beckman 755 analyzers.

4.3 PROCESS/SOIL SAMPLE COLLECTION PROCEDURES

Process samples will be collected during the Tier 4 testing to determine the presence of dioxin and dioxin precursors in feed streams to the combustion device and the presence of dioxins in nongaseous effluent ash streams from the combustion device or the collected particulate from the emission control device. Soil samples will also be collected for dioxin analysis to provide information on the dioxin content (if any) in the soils in the plant vicinity. All analyses for the presence of dioxin will be conducted by Troika. The precursor analyses will be conducted at Radian's RTP laboratories.

The types of samples to be collected will include liquids, slurries, sludges, and solids. The samples that will be collected at each site will vary depending on the type of combustion device and emission control equipment. Examples of the types of feed and effluent streams to be sampled and the preferred methods of sampling these streams are discussed briefly in this section. Container preparation and sampling frequencies/quantities are also discussed. Further details on each method are given in "National

Dioxin Study Tier 4 - Combustion Sources: Sampling Procedures" (5). The actual streams to be sampled at each site will be documented in the site-specific test plans which will be reviewed by the EPA Project Officer prior to testing. General quality control procedures which apply to the collection of all process/soil samples are discussed in Section 9.3 of this document.

4.3.1 Liquid/Slurry Streams and Sampling Techniques

Examples of liquid/slurry streams that may be sampled during this program include fuels, bottom ash slurries, cooling or process water, scrubber blowdown, and demister blowdown. Available liquid/slurry sampling techniques are summarized in Table 4-4. Whenever possible, liquid/slurry grab samples will be collected using the tap sampling method at a location where the sample is moving through a pipe. If the liquid stream cannot be sampled by this technique, the most appropriate of the other techniques listed in Table 4-4 will be used.

To acquire the tap sample, the outlet of the valve or stopcock used for sample removal will be fitted with a length of precleaned Teflon® tubing sufficiently long to reach the bottom of the sample container as shown in Figure 4-7. After the Teflon® conduit line has been placed in the sample container, the tap will be opened to admit a moderate flow of liquid. The conduit line, but not the sample container, will be flushed before the sample is actually taken. Moving liquid streams, known to contain particulate matter or immiscible phases, will be considered stratified. The optimum location for the sampling tap will be after a bend of constriction which will induce turbulence or at least promote mixing.

4.3.2 Sludge/Solid Samples and Sampling Techniques

Examples of solids/sludges that may be sampled during this program include fuels, bottom ash, pollution control device solids, and soils from the plant. Available sampling techniques and their applicability are shown in Table 4-5. Tools used for these methods are shown in Figures 4-8 through 4-14. The preferred sampling method for process solids and sludges will depend on site specific factors, and the method to be used will be documented in the test plan. Soils will be sampled using a bulb planter.

TABLE 4-4. SUMMARY OF LIQUID/SLURRY SAMPLING TECHNIQUES

Technique	Description
Tap Sampler	Appropriate for homogeneous flowing liquids in pipes or ducts.
Dipper	Surface liquid sampling device or outflow of pipe of sluiceway.
Coliwasa	Sampler which will collect liquid from standing liquids contained in drums, tanks, pits, or lagoons.
Weighted Bottle	Subsurface liquid sampling device.

TABLE 4-5. SOLID/SLUDGE/SOIL SAMPLING METHODS AND APPLICATIONS

Method	Applicable to			Comments
	Solids	Sludges	Soils	
Stopped belt cut	X	X		For conveyer systems
Thief	X			For flowable, granular material
Trier	X			For granular material
Auger	X	X	X	For hard, solid material
Dredge	X	X	X	For sludge pits
Trough	X	X		For end of conveyer
Dipper/scoop	X	X		For end of pipe sampling
Bulb Planter			X	For soils

X = Applicable.

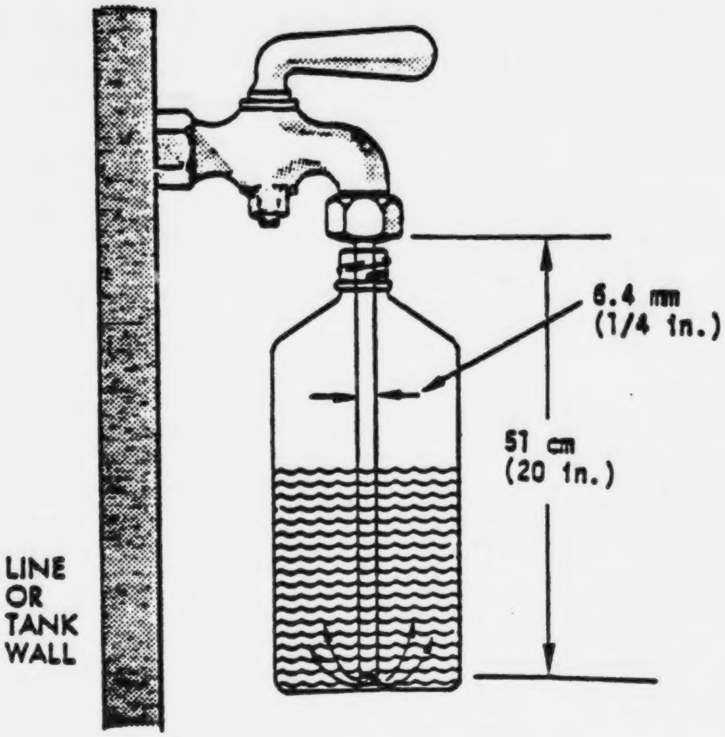

6.4 mm
(1/4 in.)
51 cm
(20 in.)
LINE
OR
TANK
WALL

Figure 4-7. Schematic of tap sampling.

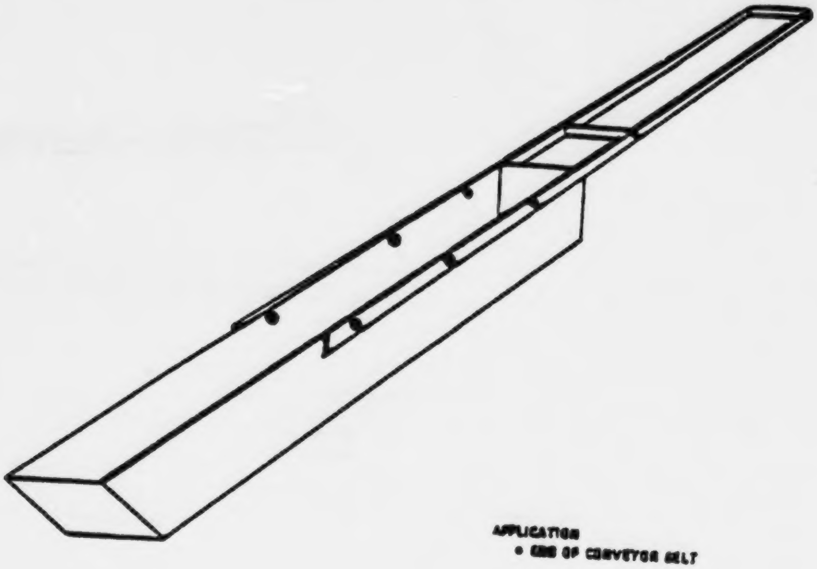

APPLICATION
• END OF CONVEYOR BELT

Figure 4-8. Sampling trough.

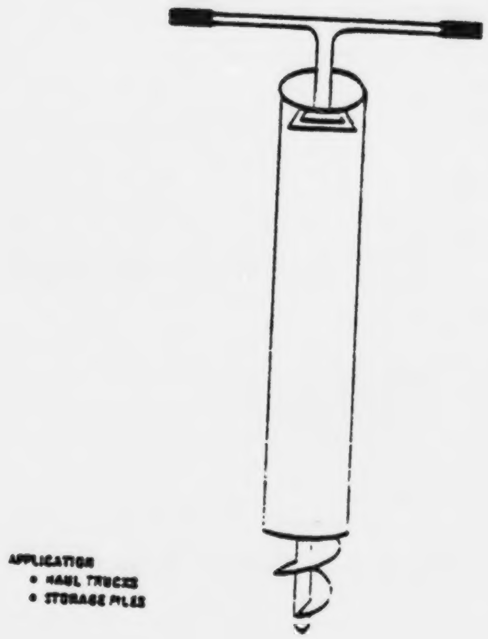
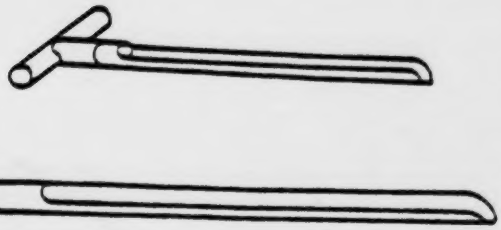
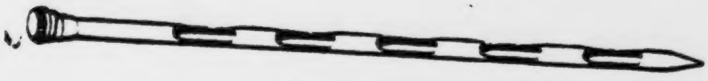

APPLICATION
• HAUL TRUCKS
• STORAGE PILES

Figure 4-9. Sample auger.



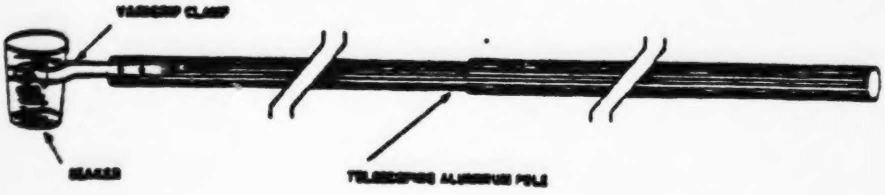
APPLICATION
- STORAGE PILES
- SAMPLING PORTS
- POKE HOLES

Figure 4-10. Sample triers



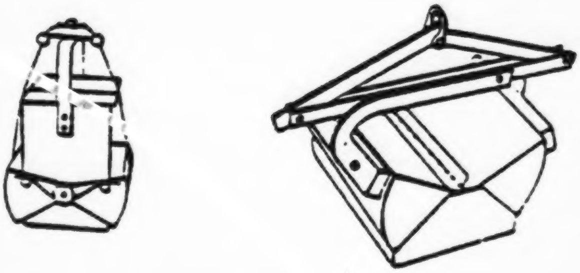
APPLICATION
- STORAGE PILES
- SAMPLING PORTS
- POKE HOLES

Figure 4-11. Sample probe or thief.


VARIGRIP CLAMP
BEAKER
TELESCOPING ALUMINUM POLE

APPLICATION
- END OF PIPE SAMPLING
- THICKENERS
- SETTLING BASINS [illegible]

Figure 4-12. Dipper.



APPLICATION
- SETTLING BASINS
- THICKENERS, CLARIFIERS
- [illegible]

Figure 4-13. Dredge samplers

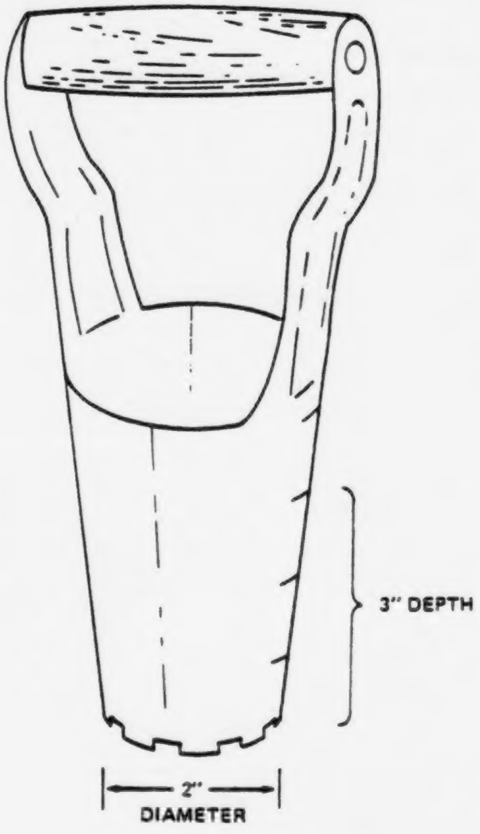

3" DEPTH
2"
DIAMETER

Figure 4-14. Bulb Planter

The procedure to be used for selecting the sampling locations will be based on the "Sampling Guidance Manual for the National Dioxin Study" (6). The various sludge/solid sampling techniques are discussed briefly below.

4.3.2.1 ASME "Stopped-Belt Cut" Method (D2234-76). This method will be used for sampling of solid materials transported on conveyor belts that can be stopped for an appreciable amount of time without disrupting plant operations (i.e., several minutes). The method is applicable to feed solids, dry bottom ash, char or slag, and sludge.

This is the most favorable method for obtaining a representative sample of material on a conveyor belt. With the belt stopped, a full-stream cut will be obtained from the belt with a shovel and brush (for fine material). The width of the cut must be at least three times the diameter of the largest particle or 1.25 inches, whichever is greater. Also, the sides of the cut must be as nearly parallel as possible.

4.3.2.2 Thief, Trier, or Auger Sampling of Stationary Materials (D2234-76, C311-77, D346-78. These methods will be used for sampling of solid materials located in hoppers, storage piles, rail cars or trucks, or other stationary containers. The methods apply to feed solids, bottom ash/slag, fly ash, and soil.

Three possible methods are available for sampling stationary materials: D2234-76 for solids and other lumped materials, D346-78 for solids or any material in hopper cars or trucks, and C311-77 for fly ash and other granular materials (except pulverized coal).

The first method involves taking a prescribed number of increments of the material from systematically or randomly located points throughout the volume of the pile or hopper. Points that are selected systematically are preferred. The material can be shoveled from the pile, but augers or slotted pipes (thiefs) are more useful when it is necessary to remove material from the interior of a pile.

Method D346-78 is very similar to D2234-76 but also includes a useful diagram for selecting sampling points in a loaded hopper car or dump truck. It is expected that access to certain waste materials may be restricted until after they are loaded into rail cars or trucks. Therefore, this method may be used for selected sampling points on any material so stored.

Method C311-77 involves taking grab or composite samples of granual material in bulk storage or in rail cars or trucks. Samples are to be withdrawn from the entire volume of material from "well distributed" points over the area of storage.

4.3.2.3 Dipper/Scoop. Grab samples of sludge material may be collected if access to a sluiceway is available. To take a grab sample with a dipper, the dipper will be cleaned, mounted on a telescoping pole, and inserted into the stream at the desired depth with the mouth of the container down. The dipper will be turned over to an upright position, allowing the container to fill completely. The dipper will then be removed from the sludge, and the sample transferred to a temporary storage container. This process will be repeated until sufficient increments have been collected.

4.3.3 Sample Container and Equipment Preparation

Sampling containers and sampling equipment will be cleaned prior to testing according to the procedure listed in Table 4-6. The cleaned glassware will be transported to the sampling location with the Teflon® lids tightly in place. Once the sample is introduced to the container, the lid shall be replaced and wrapped with Teflon® tape, wrapped in cleaned foil, and transported to the sampling locations. Between sampling at the same location, no extra cleaning is necessary. When going to a new location with the same equipment, the cleaning shall consist of:

1. Removal of loose sample,
2. H_2O rinse (x3),
3. Acetone rinse (x3) (pesticide grade),
4. Methylene Chloride rinse (x3) (pesticide grade),
5. Air dry in a clean environment, and
6. Foil wrap (methylene chloride rinsed).

4.3.4 Sampling Frequency and Quantities

Process sampling will be conducted concurrently with the Modified Method 5 sampling for dioxin. The sampling frequency will vary depending on

TABLE 4-6. PRETEST CLEANING PROCEDURE FOR SAMPLING CONTAINERS AND EQUIPMENT

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

1. Soak all glassware in hot soapy water (Alconox) 50°C or higher.
2. Distilled/deionized H_2O rinse (X3)[a].
3. H_2O rinse (X3).
4. Chromerge rinse if glass, otherwise skip to 6.
5. High purity liquid chromatography grade H_2O rinse (X3).
6. Acetone rinse (X3), (pesticide grade).
7. Methylene chloride[b] rinse (X3), (pesticide grade).
8. Oven dry (110°C - HR).
9. Cap containers with Teflon lids. Foil wrap the sampling equipment.

---

[a] X3 = three times

[b] For Sites 01 through 04 hexane was used instead of methylene chloride for this final solvent rinse.

the specific sample being taken. Combustion device feed samples, such as liquid, solid, or sludge fuels, will be sampled hourly whenever possible. Other samples, such as bottom ash or control device solids, may be taken less frequently especially if plant personnel are needed to assist the sampling due to safety or process considerations.

Individual process samples will be composited at the end of each test run. When possible, samples of streams known to have widely varying flow and composition will be composited on a weighted basis. Sufficient sample will be collected to provide two 500 g composite samples for each combustion device feed stream. One of the samples will be sent to Troika for dioxin analysis, and the other will be analyzed for dioxin precursors at Radian's RTP laboratory. Composite samples of the combustion device fuel(s) and/or other selected process samples (125 ml of each) will also be sent to Radian Analytical Services (Austin, Texas) for determination of total chlorine by Parr Bomb combustion followed by ion chromatography. One duplicate fuel sample will also be sent to Radian Analytical Services per test site for quality control purposes.

Sufficient sample will be collected to provide a 500 g composite sample of any material sample downstream of the combustion device (e.g., bottom ash, fly ash, or scrubber blowdown). These samples will be sent to Troika for dioxin analysis. A 500 g composite of soil sample will also be sent to Troika for dioxin analysis.

4.4 PROCESS DATA COLLECTION

In addition to the collection of flue gas and liquid/solid process samples, data on a number of process parameters will also be obtained during the Tier 4 dioxin emission tests. These parameters include mass flow rates of liquid, solid, or gaseous fuels fed to the combustion device, combustion or excess air usage, flue gas temperatures and pressures, heat or steam generation rates, scrubber water flow rates, and any other available data that provide an indication of (1) the combustion device, or (2) the emission control device operating conditions.

The actual process data to be collected during each test will depend on the particular type of combustion device and emission control equipment. The required data will usually be available from plant instrumentation, but it may be necessary to measure and/or estimate certain parameters in some instances. The data to be collected and the methodology to be used in obtaining the data will be documented in the site-specific test plan, which will be reviewed by the EPA Project Officer prior to testing.

SECTION 5

LABORATORY ANALYTICAL PROCEDURES

Laboratory analyses to be conducted for this program at Radian Laboratories include: 1) the determination of dioxin precursors in the process and combustion air XAD samples, 2) the determination of HCl concentrations in the impinger catch from the HCl sampling trains, and 3) the determination of total elemental chlorine in selected process samples. All analyses for dioxins will be conducted by Troika. The dioxin precursors to be quantified include chlorophenols, chlorobenzenes, and polychlorinated biphenyls. These compounds will be quantified by gas chromatography/mass spectrometry (GC/MS). HCl concentrations will be determined by ion chromatography. Total elemental chlorine for fuels will be determined by Parr bomb combustion followed by ion chromatography. The procedures to be used for these analyses are discussed below. It should be noted that the general procedures outlined in this section for precursor sample preparation may require modification for different types of process samples, for example makeup water vs. sewage sludge. All procedural changes will be documented in the site-specific test reports.

5.1 DIOXIN PRECURSOR DETERMINATION

The analytical procedures for the determination of chlorophenols (CP), chlorobenzenes (CB), and polychlorinated biphenyls (PCB) in process and/or resin samples will entail initial extraction or dilution of the various samples with organic solvents, preliminary separations of the compounds of interest using partitioning and liquid chromatography and analyses of the various processed extracted fractions using coupled gas chromatography/mass spectrometry (GC/MS). All of the compounds of interest may be injected directly into the GC/MS.

5.1.1 Instrumentation.

The instrumentation used to perform quantitative analyses for the compounds of interest includes a gas chromatograph coupled through an interface to a mass spectrometer equipped with a data system (GC/MS/DS). The gas chromatograph is equipped with split/splitless and on-column injectors and with a fused-silica capillary column. The mass spectrometer (Finnigan 4023 GC/MS/DS) is operated under the control of the computer-based data system. Each of the groups of chlorocarbons of interest (CP, CB, and PCB) is analyzed separately.

Due to the nature of GC/MS instrumentation and the cost associated with sample analysis, pre-screening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or gas chromatography/Hall detection (GC/HD) will be conducted to provide information regarding the complexity and concentration level of the sample, as well as halogenated compound content, prior to GC/MS analysis. The pre-screening will be accomplished by using either capillary columns or less expensive packed columns. The mass spectrometer will be operated in a full mass range (40 to 450) scanning mode for most of the analyses. The range for which data is acquired in a GC/MS run will be sufficiently broad to encompass the major ions for each of the surrogate spikes and internal standards.

5.1.1.1 GC Conditions.

The GC will be equipped with a fused silica capillary column for compound separation. Fused silica columns provide the compound separation often necessary for the quantitation of a complex sample. Additionally, the inertness of the column itself greatly improves the versatility of the analytical system for samples that contain both polar and non-polar compounds. The conditions for the GC are given below.

Column: 30 M fused silica capillary, coated with SE-54 or equivalent.

Injection Temperature: 280°C.

Column Temperature: 25°C for 4 minutes then 25-270°C @ 10°/minute. Hold at 270°C until no evidence of eluting peaks.

Carrier Gas: High purity He flowing @ 3 mL/minute.

Injection Volume: 1 uL.

Electron Energy: 70 ev (nominal).

The temperature program will be changed if required to accomplish a difficult separation.

5.1.1.2 MS Conditions.

In general, the cycle time between collections of complete mass spectra will be selected to be compatible with elution of the components in the sample. For capillary column GC separations, the cycle time will be on the order of one second. Longer cycle times may lead to distortion of the spectra. For best characterization of a GC peak, at least five spectra should be collected across the peak. For low level components in the extracts, the elution peak may be less than 3 seconds wide and it might not be possible to collect enough scans to characterize the GC peak.

To insure consistency with compendia of mass spectra, the instrumentation will be tuned to meet the special criteria for decafluorotriphenylphosphine. The criteria for the tuning requirements are shown in Table 9-2.

Typical MS conditions are given as follows.

Instrument:	Finnigan 4023/Incos.
Scan Range:	35 to 450 amu.
Scan Rate:	1 cycle/second.

5.1.2 Preparation of Sample for Analysis.

Sample preparation will generally involve extraction of the process sample or resin with solvents followed by concentration of the extract prior to GC or GC/MS analysis. Certain sample types may also require fractionation by column chromatography if the samples are contaminated with compounds that will interfere with the precursor analysis.

Prior to sample preparation, the sample quantity will be measured and appropriate quantities of surrogate compounds will be added to the samples. These compounds will be selected so that a measure of precursor recovery from the samples can be made. Quantitation standards will be added immediately prior to analysis.

Details of the extraction and fractionation procedures to be used for sample preparation are provided in the sections below. A flow chart for sample preparation and pre-screening is shown in Figure 5-1.

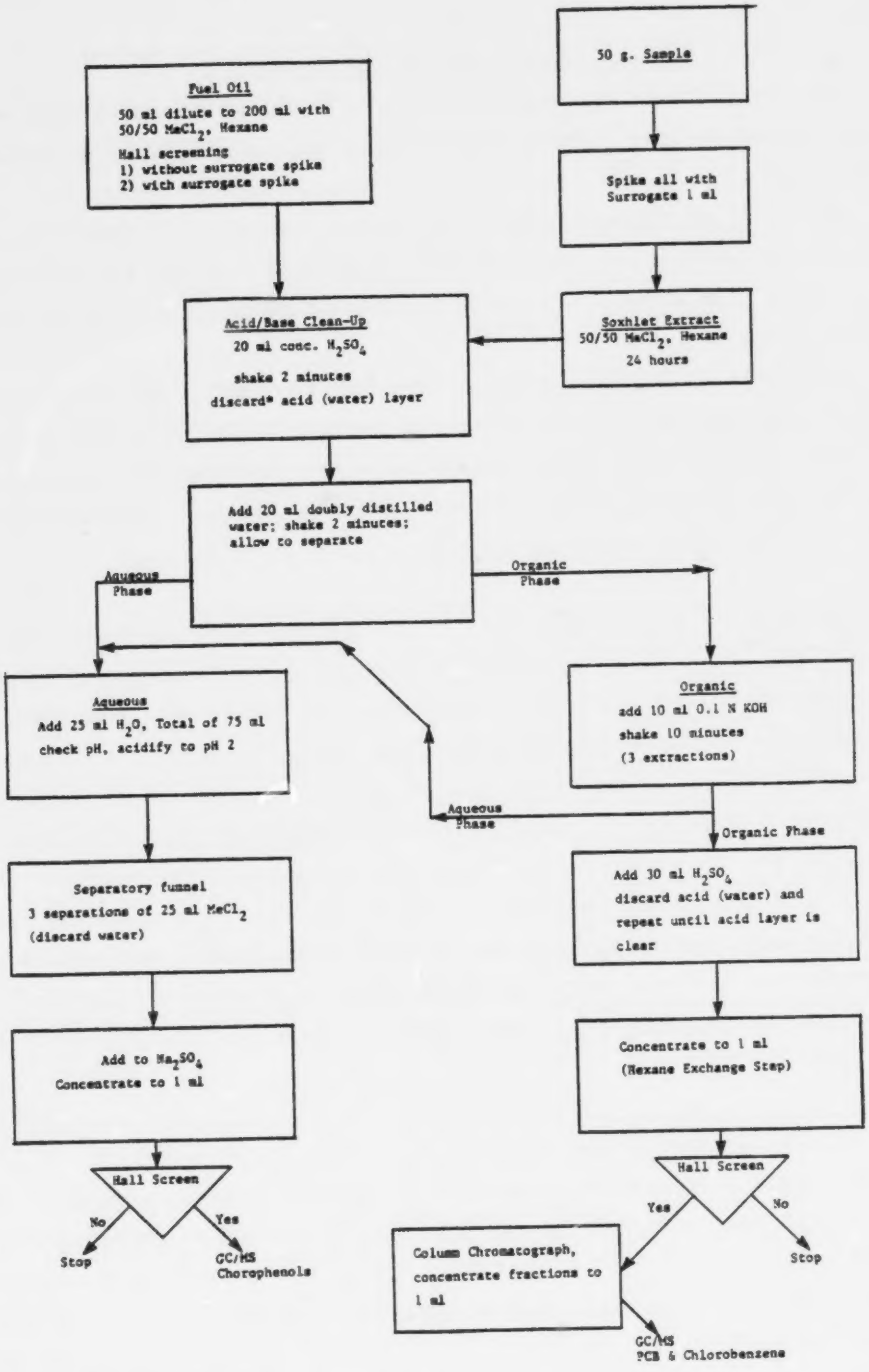
5.1.2.1 Sample Extraction.

A scheme of acceptable extraction methods and solvents arranged by type of sample matrix will be developed. Resin samples and sludges will be Soxhlet extracted by hexane/$MeCl_2$ or methanol.

5.1.2.2 Fractionation and Concentration of Sample Extracts.

Fractionation or cleanup procedures may not be required for extracts from a relatively clean sample matrix. However, most sample types will require some cleanup. Cleanup must be performed if any of the following conditions are observed.

1. Interferences prevent observation or measurement of the isotopically labeled compounds;
2. Interferences are present in the retention time window at any of the ions characteristic of the target analytes;
3. The required detection limit cannot be achieved; and
4. The sample extract is dark colored and viscous.


Fuel Oil
50 ml dilute to 200 ml with
50/50 $MeCl_2$, Hexane
Hall screening
1) without surrogate spike
2) with surrogate spike
50 g. Sample
Spike all with
Surrogate 1 ml
Soxhlet Extract
50/50 $MeCl_2$, Hexane
24 hours
Acid/Base Clean-Up
20 ml conc. H_2SO_4
shake 2 minutes
discard* acid (water) layer
Add 20 ml doubly distilled
water; shake 2 minutes;
allow to separate
Aqueous Phase
Organic Phase
Aqueous
Add 25 ml H_2O, Total of 75 ml
check pH, acidify to pH 2
Organic
add 10 ml 0.1 N KOH
shake 10 minutes
(3 extractions)
Aqueous Phase
Organic Phase
Separatory funnel
3 separations of 25 ml $MeCl_2$
(discard water)
Add 30 ml H_2SO_4
discard acid (water) and
repeat until acid layer is
clear
Add to Na_2SO_4
Concentrate to 1 ml
Concentrate to 1 ml
(Hexane Exchange Step)
Hall Screen
No
Yes
Stop
GC/MS
Chorophenols
Hall Screen
Yes
No
Stop
Column Chromatograph,
concentrate fractions to
1 ml
GC/MS
PCB & Chlorobenzene

*Discard means save separately

FIGURE 5-1. Flow chart for precursor sample preparation and pre-screening

5.1.2.3 Acid/Base Cleanup and Partitioning.

Heavily contaminated samples may require preliminary cleanup prior to column chromatography. For those situations, the following procedures will be followed.

Add 20 mL of concentrated H_2SO_4 to the bottle containing the sample extract, cap the vessel, and shake for 2 minutes. Allow the mixture to stand; after the aqueous and organic layers separate completely, remove and discard the acid layer.

Add 20 mL of doubly distilled water to the bottle containing the sample extract, cap the vessel, and shake for 2 minutes. Allow the bottle to stand until the aqueous and organic layers separate; transfer the aqueous layer to a clean 60-mL bottle equipped with a Teflon®-lined cap. Retain this aqueous layer for subsequent analysis for CP.

Add 10 mL of 0.1 n KOH to the organic layer and extract the chlorinated phenols from the sample by shaking the mixture for 10 minutes. Transfer the base layer to the sample bottle containing the water wash from above.

Repeat the case extractions two more times, combining all base extracts in the one bottle. Reserve the base extracts for analysis of chlorophenols. Continue with cleanup of organic phase for remaining organic constituents.

Using the same procedures as applied above, wash the extract successively with 30-mL portions of concentrated H_2SO_4 and doubly distilled water, in each case discarding the water or acid layer. The acid washing procedures are repeated until the acid layer is virtually colorless. Concentrate to approximately 1 mL under a stream of dry nitrogen in water bath (55°C).

5.1.2.4 Column Chromatography.

Prepare a glass macro-column, 20 mm o.d. x 230 mm in length, taper to 6 mm o.d. on one end. Pack the column with a plug of silanized glass wool, followed successively by 1.0 g silica, 2.0 g silica containing 33% (w/w) 1 M NaOH, and 2.0 g silica. Quantitatively transfer the concentrated extract to the column and elute with 90 mL hexane. Collect the entire eluate and concentrate to a volume of 1 mL in a centrifuge tube, as above.

Construct a disposable liquid chromatography mini-column by cutting off a 5-mL Pyrex® disposable pipette at the 2.0 mL mark and packing the lower portion of the tube with a small plug of silanized glass wool, followed by 1 g of Woelm basic alumina, which has been previously activated for at least 16 hours at 600°C in a muffle furnace and cooled in a desiccator for 30 minutes just before use. Quantitatively transfer the concentrate from above onto the liquid chromatography column, rinse the centrifuge tube consecutively with two 0.3-mL portions of 3 percent CH_2Cl_2:hexane, and transfer the rinses to the chromatography column.

Elute the column with 7 mL of 3 percent (v/v) CH_2Cl_2:hexane and retain the elute for analyses of PCB and chlorobenzenes.

Elute the column with 20 mL of 50 percent (v/v) CH_2Cl_2:hexane and retain the eluate for analyses of PCDD and PDF.

5.1.2.5 Concentration of Samples.

Concentrate each of the retained fractions to a volume of approximately 1 mL by heating the tubes in a water bath while passing a stream of prepurified N_2 over the solutions, as described above. Quantitatively transfer the concentrated fractions into separate 2-mL micro-reaction vessels. Evaporate the solutions in each of the micro-reaction vessels almost to dryness, using the procedures just mentioned; rinse the walls of each vessel with 0.5 mL CH_2Cl_2; and reconcentrate just to dryness.

Approximately 1 hour before GC/MS analysis, dilute the residue in each micro-reaction vessel with an appropriate quantity of solvent (depending on the anticipated quantities of analytes in each vessel) and gently swirl the solvent in the vessel to ensure dissolution of PCB and chlorobenzene.

5.1.2.6 Acetylation (Chemical Preparation) of Sample Extracts for CP Analysis.

Previous experience in Radian's RTP Laboratory has demonstrated that reproducible quantitative measurements for CP are extremely difficult to obtain without derivatization. For analysis of CP, the following derivatization procedure will be used. The derivatization sequence described below will be tested on a series of chlorophenols, and adjustments in the conditions will be made to insure that conversion is quantitative. Control will be exercised to see that derivatization conditions, once optimized, are maintained as nearly constant as possible. With a large excess of derivatizing agent and vigorous reaction conditions, it should be possible to obtain quantitative conversion and accurate analytical measurements.

Add 25 mL of doubly distilled water and check the pH of the solution from the base extractions with pH paper. Add HCl if necessary to adjust pH to 2.

Add 25 mL of methylene chloride layer to the acidified mixture and agitate the sample for 10 minutes using a wrist-action shaker and allow the mixture to stand until complete separation of layers occurs (centrifuge if necessary).

Transfer the 60-mL flint glass bottle (fitted with a Teflon®-lined cap) that contains approximately 2 g of anhydrous Na_2SO_4.

Repeat the methylene chloride extraction step two more times, combining all extracts and then shake the bottle to dry the methylene chloride solution.

Transfer approximately 10 mL of the methylene chloride solution into a 16 x 100 mm screw-capped test tube fitted with a Teflon®-lined cap.

Concentrate the solution in the tube to a volume of approximately 1 mL by passing a stream of purified N_2 over the surface of the liquid, while applying gentle heat (50°C) to the test tube. Add more of the solution and continue to concentrate until all of the solution has been transferred and concentrated.

Add 5 mL of methylene chloride to a 60 mL bottle containing Na_2SO_4, shake to rinse the bottle, and transfer the methylene chloride into the test tube containing the previously concentrated solution. Concentrate as above to approximately 1 mL.

Add 2.0 mL isooctane, 2.0 mL acetonitrile, 25 uL pyridine, and 10 uL acetic anhydride to the test tube containing the extract and agitate for 5 minutes on a wrist-action shaker.

Add 6 mL of 10 mM H_3PO_4 to the test tube and agitate for 2 minutes on a wrist-action shaker.

Remove the organic layer and concentrate it in a Reacti-Vial® at room temperature (using prepurified N_2).

5.1.3 Reagents, Chemicals, and Standards.

This section includes selected reagents and standards to be used in the analytical procedures.

5.1.3.1 Reagents and Chemicals.

1. Potassium hydroxide, anhydrous sodium sulfate, pyridine, acetic anhydride, hydrochloric acid and sulfuric acid, reagent grade;
2. Methanol, hexane, methylene chloride, benzene, acetonitrile, toluene, isooctane, "Distilled in Glass" quality obtained from Burdick and Jackson (Muskegon, Michigan) or equivalent;
3. Woelm basic alumina (activity grade I) or its equivalent;
4. Silica (Bio-Sil A);
5. Doubly distilled water obtained from an all-glass distillation apparatus;
6. Prepurified nitrogen; and
7. High-purity helium.

5.1.3.2 Standards.

The various chlorocarbon standards listed below will be utilized to perform these analyses.

Chlorinated Biphenyls (PCB)

a. 4-chlorobiphenyl (Ballachmiter No. 3);
b. 3,3'-dichlorobiphenyl (11);
c. 2,4'5-trichlorobiphenyl (31);
d. 3,3'4,4'-tetrachlorobiphenyl (77);
e. 2,2'6,6',-tetrachlorobiphenyl (54);

f. 2,3,4,5,6-pentachlorobiphenyl (116);
g. 2,2'4,5,5'-pentachlorobiphenyl (101);
h. 2,2'4,4',5,5'-hexachlorobiphenyl (153);
i. 2,2'3,4,4'5',6-heptachlorobiphenyl (183);
j. 2,2'3,3',4,4',5,5'-octachlorobiphenyl (194);
k. 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl (207);
l. 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (209);
m. 3-bromobiphenyl
n. 2,2',5,5'-tetrabromobiphenyl
o. 2,2',4,4',6,6'-hexabromobiphenyl

Chlorinated Bezenes (CB)

a. 2,4-dichlorobenzene;
b. 2,3,5-trichlorobenzene;
c. 1,2,3,5-tetrachlorobenzene;
d. pentachlorobenzene;
e. hexachlorobenzene; and
f. dichlorobenzene-d.

Chlorinated Phenols (CP)

a. 3,5-dichlorophenol
b. 2,4,5-trichlorophenol
c. 3,4,5-trichlorophenol
d. 2,3,5,6-tetrachlorophenol
e. pentachlorophenol

5.2 HCL AND CHLORIDE CONCENTRATION DETERMINATIONS

Ion chromatography (IC) will be used to determine chloride (CL^-) ion concentrations in the HCl acid train samples and selected process samples. Some acid train samples, such as those from black liquor recovery boilers, will also require determination of sulfate (SO_4^{--}) ion by IC and sodium (Na^+) ion by atomic absorption (AA) spectroscopy.

Analytical conditions for the IC analysis will be as follows:

Chromatograph: Ion/chromatograph, Dionex® or equivalent

Column: 250 mm anion separator column and an anion suppressor

Eluent: 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 aqueous solution

Detector: Electrical Conductivity Detector

Regenerant: 1 N aqueous H_2SO_4 solution

For anion analysis, the eluent (0.003 M $NaHCO_3$/0.0024 M Na_2CO_3) and separator column (containing anion resin in the HCO_3^-/CO_3^{2-} form) cause the sample ions to split into distinct bands. The retention time of each anion is influenced by the affinity of that ion, the eluent used, column length, and the eluent flow rate. The effluent from the separator column is then fed to the suppressor column. Two reactions occur in the suppressor column. The resin (a strong acid resin/H^+ form) removes Na^+ and protonates the HCO_3^-/CO_3^{2-} to H_2CO_3. Then, all the sample anions exit the suppressor column as the acid since the sample cations are exchanged for H^+ in the suppressor. Quantitative results will be calculated using a linear regression obtained from a set of calibration standards.

To determine sodium ion concentrations, a sample of impinger catch will be aspirated into an air-acetylene flame through which passes a beam of electromagnetic radiation. The beam originates from an appropriate hollow-cathode lamp emitting a frequency absorbed by the ground-state (un-ionized) sodium atom. The beam then passes through a monochromater, which isolates the specific frequency and passes it to the detector. The absorbence of the unknown will be compared to that of known standards, to obtain concentration. Calibration of the IC and AA is discussed in Section 7.2.3.

5.3 TOTAL CHLORINE DETERMINATION

Fuel samples to be analyzed for total elemental chlorine will be prepared for analysis using oxygen bomb combustion as described in ASTM D2361. This procedure involves combusting approximately 0.5 grams of sample in a Parr bomb with dilute base present to absorb the chlorine vapors. The bomb contents are rinsed into a beaker with water and acidified. This solution will be analyzed for chloride content by ion chromatography using the procedures described above for HCl acid train samples.

SECTION 6

SAMPLE CUSTODY

Sample custody procedures for this program are based on EPA recommended procedures. Since samples will be analyzed in different laboratories as well as in the field, the custody procedures emphasize careful documentation of sample collection and field analytical data and the use of chain-of-custody records for samples being transported. The procedures which will be used are discussed below.

6.1 FIELD SAMPLING OPERATIONS

A team leader will be designated for the field testing effort. The team leader will be responsible for ensuring that proper custody and documentation procedures are followed for the field sampling and field analytical efforts. He will be assisted in this effort by key sampling personnel involved in sample recovery.

All sampling data, including information regarding sampling times, locations, and any specific considerations associated with sample acquisition will be recorded on preformatted data sheets. The data form for the modified Method 5 sampling is shown in Figure 6-1. The data form shown in Figure 6-2 will be used for EPA Method 5, the HCl train, and the ambient XAD train. The moisture and impinger catch data sheet is shown in Figure 6-3. Data forms to be used for liquid and solid process samples are presented in Figures 6-4 and 6-5.

Master logbooks will be used to document all sample collection activities. An example of the master logbook format which will be used is shown in Figure 6-6. The field sampling team leader will be responsible for reviewing the logbook on a daily basis and ensuring that entries are complete and up to date.

Following sample collection, all samples will be given a unique alpha-numeric (Radian) identification number. Sample labels (Figure 6-7)

MODIFIED METHOD 5 DATA

PLANT ________________
DATE ________________
SAMPLING LOCATION ________________
SAMPLE TYPE ________________
RUN NUMBER ________________
OPERATOR ________________
AMBIENT TEMPERATURE ________________
BAROMETRIC PRESSURE ________________
STATIC PRESSURE (P_s) ________________
FILTER NUMBER (s) ________________
MINIMUM SAMPLE VOLUME ________________
INITIAL LEAK CHECK ________________

PROBE LENGTH AND TYPE ________________
NOZZLE I D. ________________
ASSUMED MOISTURE, % ________________
SAMPLE BOX NUMBER ________________
METER BOX NUMBER ________________
METER Δ H@ ________________
C FACTOR ________________
PROBE HEATER SETTING ________________
HEATER BOX SETTING ________________
REFERENCE Δp ________________
DRY/GAS METER FACTOR (Y) ________________
FINAL LEAK CHECK ________________

SCHEMATIC OF TRAVERSE POINT LAYOUT
READ AND RECORD ALL DATA EVERY ______ MINUTES

Traverse Point Number	Sampling Time Min.	Clock Time (24-hr Clock)	Gas Meter Reading (V_m), ft³	Velocity Head (ΔP_s), in. H_2O	Stack T_s, °F	Orifice Pressure Differential (ΔH, in. H_2O)		Temperature °F/°C (Circle One)								Pump Vacuum in. Hg
						Desired	Actual	Probe	Filter		Recirc. Water	Absorbent Trap	Dry Gas Meter		Impinger Exit	
									Skin	Out			Inlet (T_m in)	Outlet (T_m out)		

COMMENTS

Figure 6-1. Modified Method 5 data sheet.

METHOD 5, HCl TRAIN AND AMBIENT XAD FIELD DATA

PLANT ____________
DATE ____________
SAMPLING LOCATION ____________
SAMPLE TYPE ____________
RUN NUMBER ____________
OPERATOR ____________
AMBIENT TEMPERATURE ____________
BAROMETRIC PRESSURE ____________
STATIC PRESSURE, (P_s) ____________
FILTER NUMBER (s) ____________

PROBE LENGTH AND TYPE ____________
NOZZLE I.D. ____________
ASSUMED MOISTURE, % ____________
SAMPLE BOX NUMBER ____________
METER BOX NUMBER ____________
METER $\Delta H_@$ ____________
C FACTOR ____________
PROBE HEATER SETTING ____________
HEATER BOX SETTING ____________
REFERENCE Δp ____________
METER γ ____________

SCHEMATIC OF TRAVERSE POINT LAYOUT

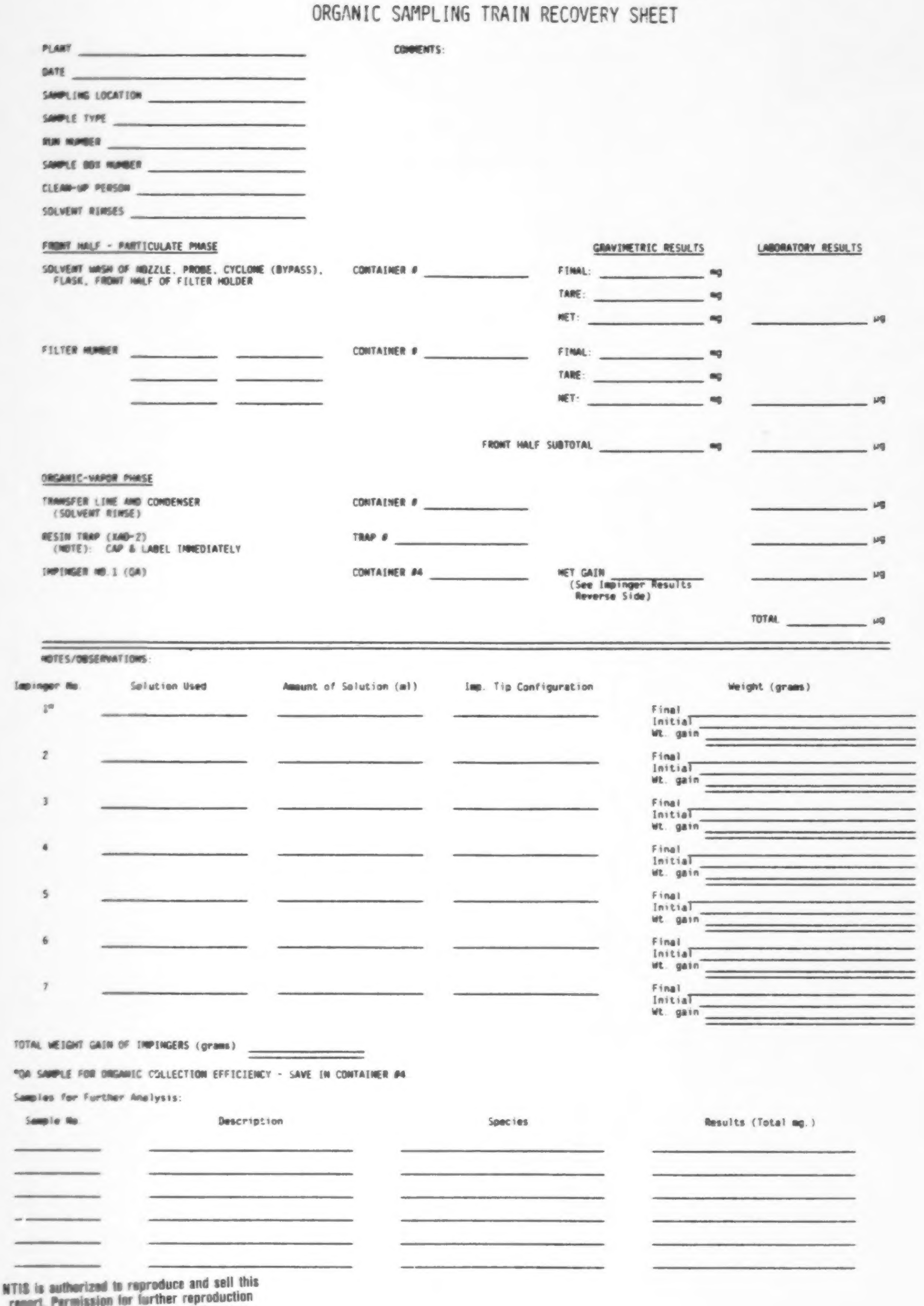
READ AND RECORD ALL DATA EVERY ________ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F			

COMMENTS

EPA (Dur) 235
4/72

Figure 6-2. Source Sampling Field Data



ORGANIC SAMPLING TRAIN RECOVERY SHEET

PLANT ____________________

DATE ____________________

SAMPLING LOCATION ____________________

SAMPLE TYPE ____________________

RUN NUMBER ____________________

SAMPLE BOX NUMBER ____________________

CLEAN-UP PERSON ____________________

SOLVENT RINSES ____________________

COMMENTS:

			GRAVIMETRIC RESULTS	LABORATORY RESULTS
FRONT HALF - PARTICULATE PHASE				
SOLVENT WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER		CONTAINER # ______	FINAL: ______ mg	
			TARE: ______ mg	
			NET: ______ mg	______ µg
FILTER NUMBER	______ ______	CONTAINER # ______	FINAL: ______ mg	
	______ ______		TARE: ______ mg	
	______ ______		NET: ______ mg	______ µg
		FRONT HALF SUBTOTAL	______ mg	______ µg
ORGANIC-VAPOR PHASE				
TRANSFER LINE AND CONDENSER (SOLVENT RINSE)		CONTAINER # ______		______ µg
RESIN TRAP (XAD-2) (NOTE): CAP & LABEL IMMEDIATELY		TRAP # ______		______ µg
IMPINGER NO.1 (QA)		CONTAINER #4 ______	NET GAIN ______ (See Impinger Results Reverse Side)	______ µg
				TOTAL ______ µg

NOTES/OBSERVATIONS:

Impinger No.	Solution Used	Amount of Solution (ml)	Imp. Tip Configuration	Weight (grams)
1*	______	______	______	Final ______ Initial ______ Wt. gain ______
2	______	______	______	Final ______ Initial ______ Wt. gain ______
3	______	______	______	Final ______ Initial ______ Wt. gain ______
4	______	______	______	Final ______ Initial ______ Wt. gain ______
5	______	______	______	Final ______ Initial ______ Wt. gain ______
6	______	______	______	Final ______ Initial ______ Wt. gain ______
7	______	______	______	Final ______ Initial ______ Wt. gain ______

TOTAL WEIGHT GAIN OF IMPINGERS (grams) ______

*QA SAMPLE FOR ORGANIC COLLECTION EFFICIENCY - SAVE IN CONTAINER #4

Samples for Further Analysis:

Sample No.	Description	Species	Results (Total mg.)
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______

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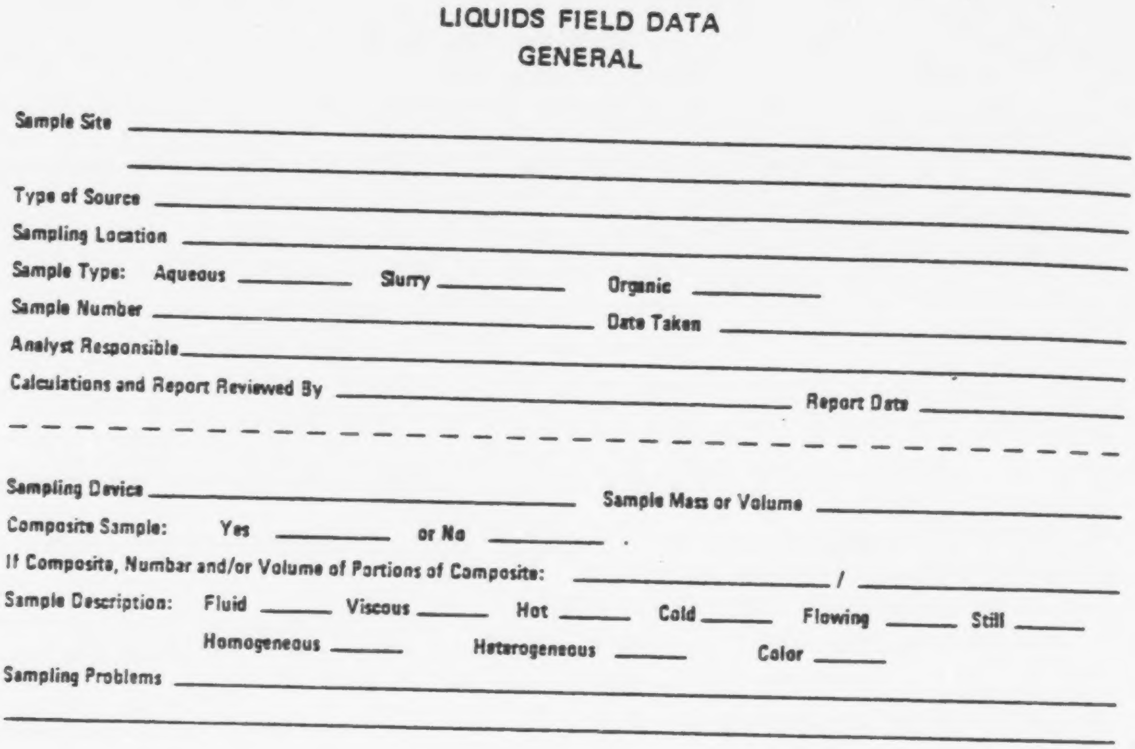
Figure 6-3. Impinger catch data sheet.



LIQUIDS FIELD DATA
GENERAL

Sample Site ____________________

Type of Source ____________________

Sampling Location ____________________

Sample Type: Aqueous ______ Slurry ______ Organic ______

Sample Number ____________ Date Taken ____________

Analyst Responsible ____________________

Calculations and Report Reviewed By ____________ Report Date ______

Sampling Device ____________ Sample Mass or Volume ____________

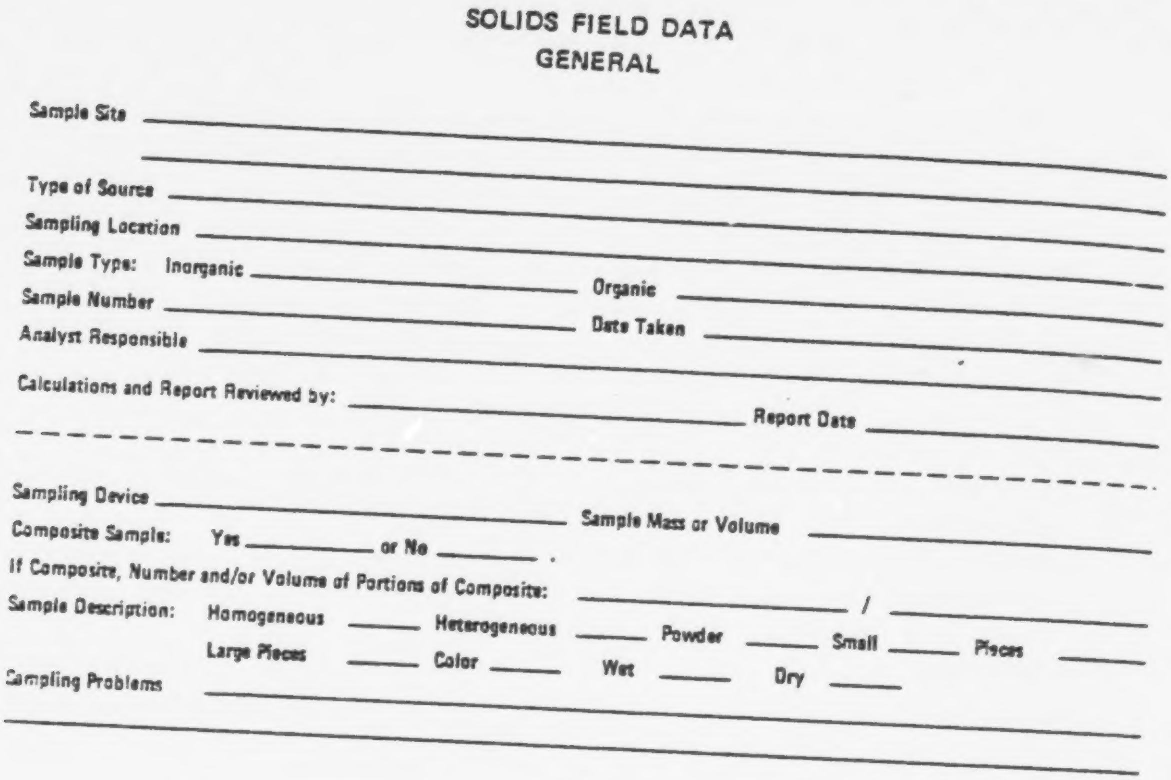
Composite Sample: Yes ______ or No ______.

If Composite, Number and/or Volume of Portions of Composite: ____________ / ____________

Sample Description: Fluid ____ Viscous ____ Hot ____ Cold ____ Flowing ____ Still ____
Homogeneous ____ Heterogeneous ____ Color ____

Sampling Problems ____________________

Figure 6-4. Process sample (liquid) field data.



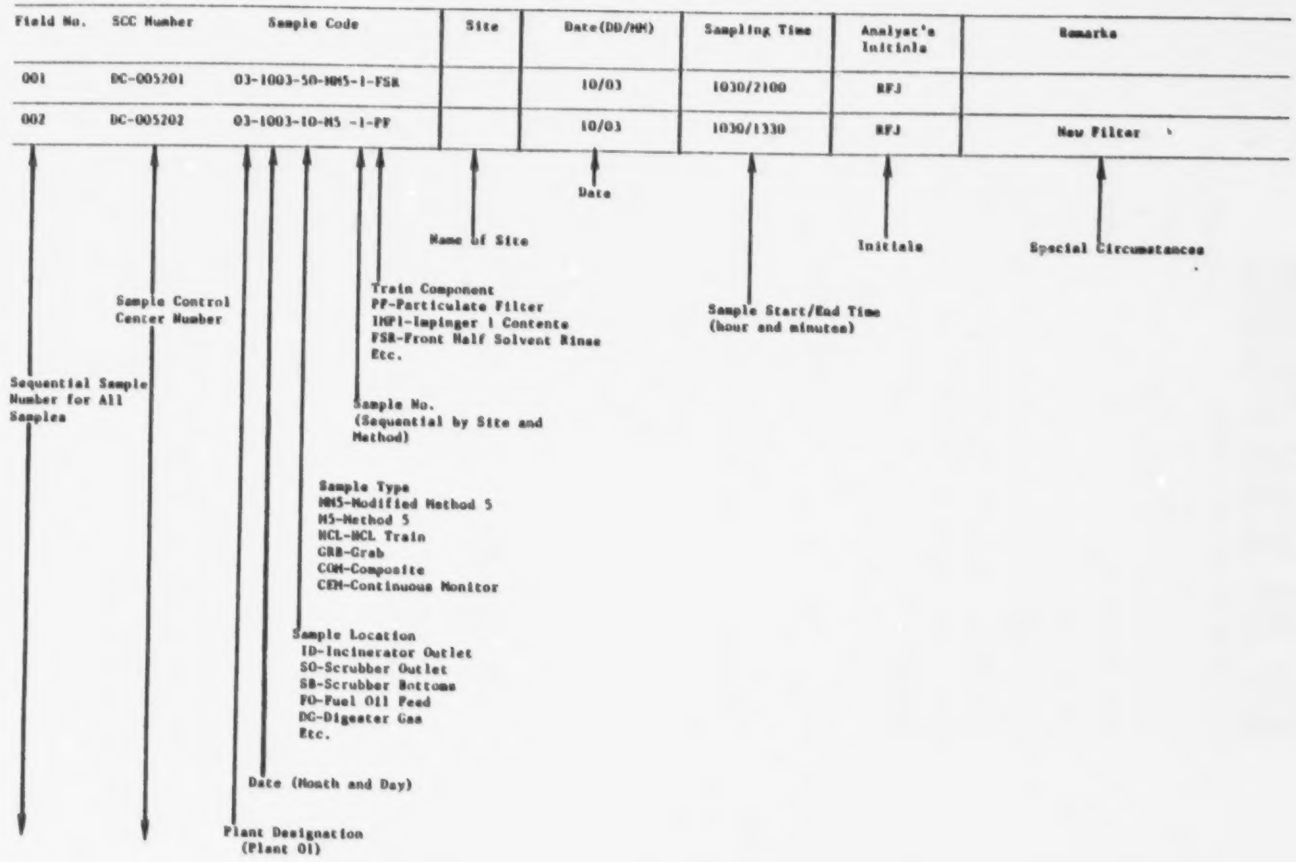
SOLIDS FIELD DATA
GENERAL

Sample Site ______________________________
____
Type of Source ______________________________
Sampling Location ______________________________
Sample Type: Inorganic ______________ Organic ______________
Sample Number ______________ Date Taken ______________
Analyst Responsible ______________________________
Calculations and Report Reviewed by: ______________ Report Date ______________

- -

Sampling Device ______________ Sample Mass or Volume ______________
Composite Sample: Yes ________ or No ________ .
If Composite, Number and/or Volume of Portions of Composite: ______________ / ______________
Sample Description: Homogeneous ______ Heterogeneous ______ Powder ______ Small ______ Pieces ______
Large Pieces ______ Color ______ Wet ______ Dry ______
Sampling Problems ______________________________
____

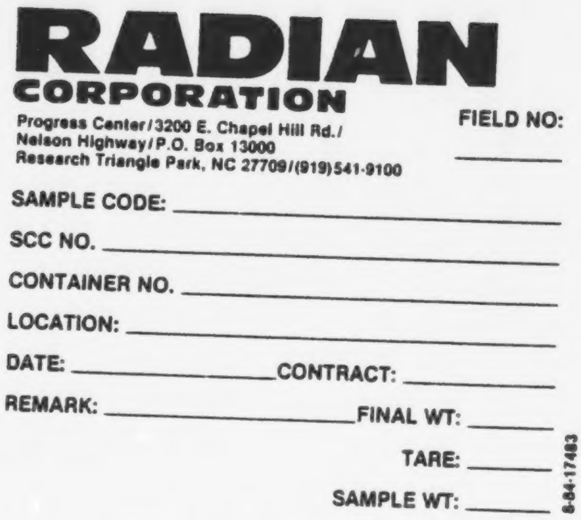
Figure 6-5. Process sample (solid) field data.



Field No.	SCC Number	Sample Code	Site	Date(DD/MM)	Sampling Time	Analyst's Initials	Remarks
001	DC-005201	03-1003-SO-MM5-1-FSR		10/03	1030/2100	RFJ	
002	DC-005202	03-1003-IO-M5 -1-PF		10/03	1030/1330	RFJ	New Filter

Sequential Sample Number for All Samples
Sample Control Center Number
Plant Designation (Plant 01)
Date (Month and Day)
Sample Location
ID-Incinerator Outlet
SO-Scrubber Outlet
SB-Scrubber Bottoms
FO-Fuel Oil Feed
DG-Digester Gas
Etc.
Sample Type
MM5-Modified Method 5
M5-Method 5
HCL-HCL Train
GRB-Grab
COM-Composite
CEM-Continuous Monitor
Sample No. (Sequential by Site and Method)
Train Component
PF-Particulate Filter
IMP1-Impinger 1 Contents
FSR-Front Half Solvent Rinse
Etc.
Name of Site
Date
Sample Start/End Time (hour and minutes)
Initials
Special Circumstances

Figure 6-6. Example of Radian Master Logbook format.



RADIAN CORPORATION

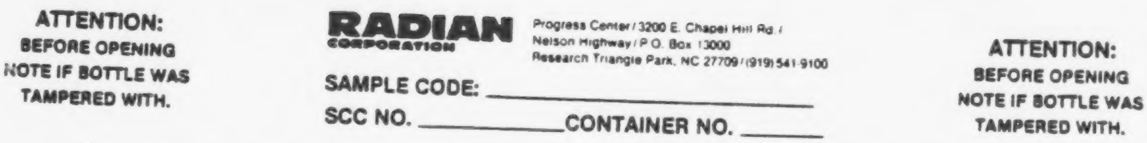
Progress Center/3200 E. Chapel Hill Rd./
Nelson Highway/P.O. Box 13000
Research Triangle Park, NC 27709/(919)541-9100

FIELD NO: ________

SAMPLE CODE: ______________________
SCC NO. ______________________
CONTAINER NO. ______________________
LOCATION: ______________________
DATE: ____________ CONTRACT: __________
REMARK: ______________ FINAL WT: ______
TARE: ______
SAMPLE WT: ______

8-84-17483

Figure 6-7. Example of Sample Lable



ATTENTION:
BEFORE OPENING NOTE IF BOTTLE WAS TAMPERED WITH.

RADIAN CORPORATION

Progress Center/3200 E. Chapel Hill Rd./
Nelson Highway/P.O. Box 13000
Research Triangle Park, NC 27709/(919)541-9100

SAMPLE CODE: ______________________
SCC NO. __________ CONTAINER NO. ______

ATTENTION:
BEFORE OPENING NOTE IF BOTTLE WAS TAMPERED WITH.

Figure 6-8. Example of Custody Seal

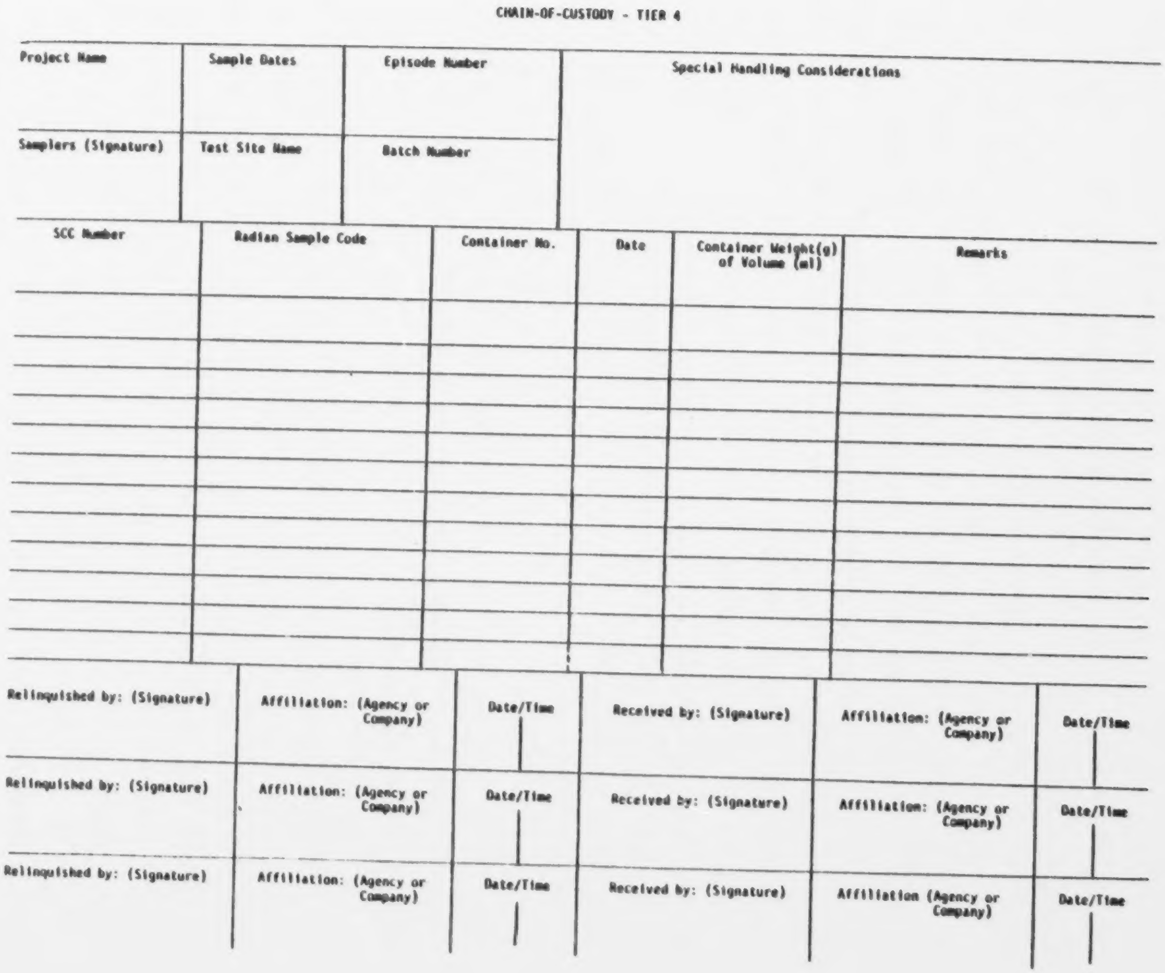
and chain-of-custody seals (Figure 6-8) will be completed and affixed to the sample container. Finally, chain-of-custody forms (Figure 6-9) will be completed by any personnel involved in the sample handling.

Samples to be analyzed for dioxin by Troika will be handled according to the procedures in the Sampling Guidance Manual for the National Dioxin Study.[1] Specific directions for documentation and shipment are attached as Appendix C. At least 2 weeks prior to the start of testing, the Sample Control Center (SCC) will be contacted through the Tier 4 SCC contact, Mr. Ed Hank [(919) 541-5575], to obtain an episode number and a set of sample control numbers for the particular test site. Changes to the sample scheduling information provided to SCC, including any change in the number or matrix of samples, sampling or shipment dates or analysis requirements, will be reported to SCC through the Tier 4 SCC contact immediately.

Each shipment of samples to Troika for a given test site will be given a batch number (#1, 2, 3, etc.) by Radian. A Dioxin Shipment Record (DSR) form (Figure 6-10) will be completed according to the instructions in Appendix B of this QAPP. All modified Method 5 train components from a single test run will be labeled with the same SCC number. However, different components of the sample will be further designated as "1 of n", "2 of n", etc. The Chain-of-Custody Record (Figure 6-9) for samples being sent to Troika will be completed and enclosed (with the DSR form) in the sample shipment container. Shipping containers will also be sealed using a chain-of-custody seal.

A letter specifying the treatment of each sample will also be enclosed in the sample shipment container. Samples or parts of samples to be combined and analyzed immediately, extracted and stored for later analysis, or simply stored as is will be clearly stated in this letter. The purpose of the letter will be to ensure that the correct samples are combined and that samples with a limited shelf life (those containing water) are extracted within the allowable time of 7 days after collection. An example of the form letter to be used is shown in Figure 6-11.

In addition to the master logbooks, daily activity logs will also be maintained by the field team leader. These will be informal logs used to



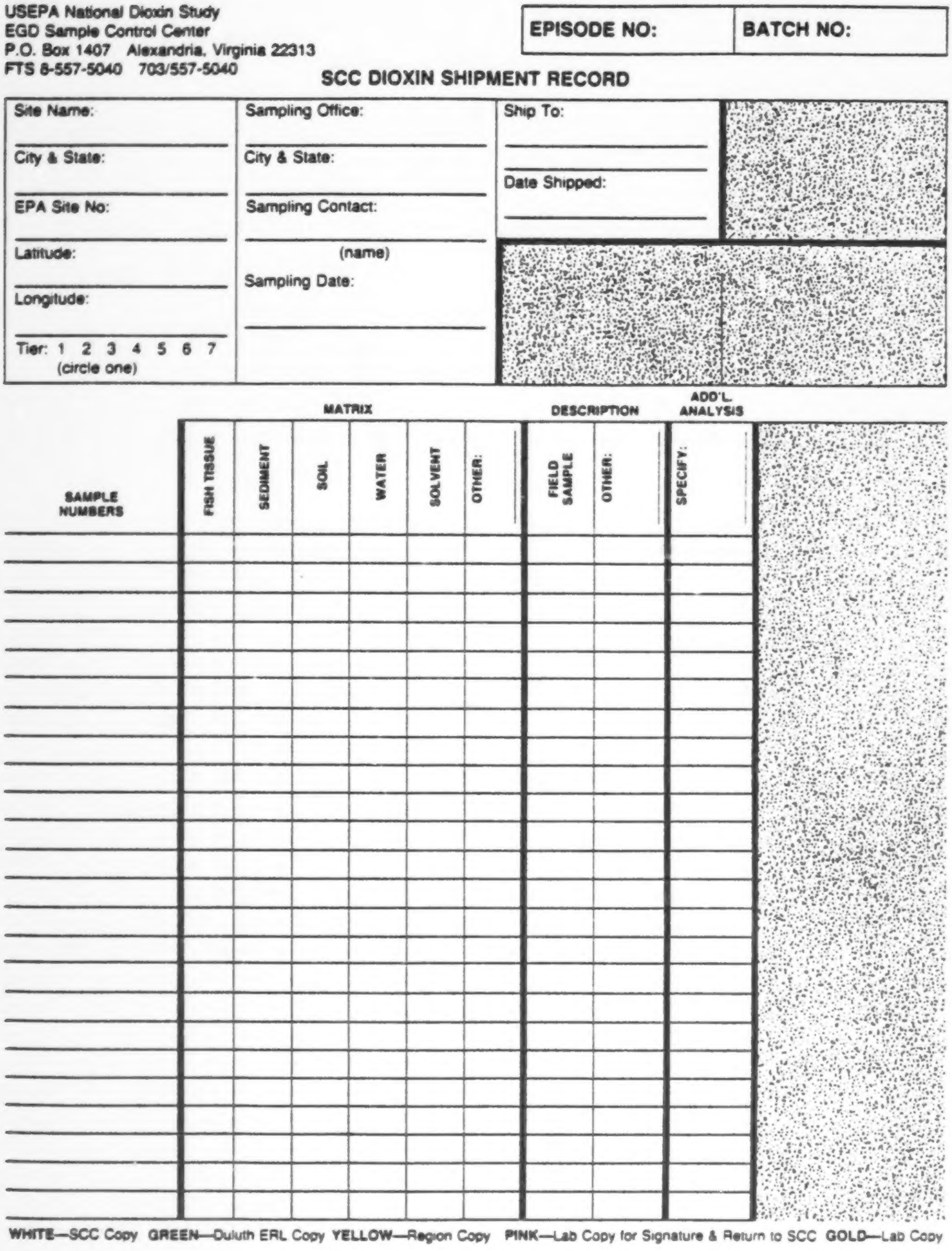
CHAIN-OF-CUSTODY - TIER 4

Project Name	Sample Dates	Episode Number	Special Handling Considerations
Samplers (Signature)	Test Site Name	Batch Number	

SCC Number	Radian Sample Code	Container No.	Date	Container Weight(g) of Volume (ml)	Remarks

Relinquished by: (Signature)	Affiliation: (Agency or Company)	Date/Time	Received by: (Signature)	Affiliation: (Agency or Company)	Date/Time
Relinquished by: (Signature)	Affiliation: (Agency or Company)	Date/Time	Received by: (Signature)	Affiliation: (Agency or Company)	Date/Time
Relinquished by: (Signature)	Affiliation: (Agency or Company)	Date/Time	Received by: (Signature)	Affiliation (Agency or Company)	Date/Time

Figure 6-9. Chain-of-Custody Form



USEPA National Dioxin Study
EGD Sample Control Center
P.O. Box 1407 Alexandria, Virginia 22313
FTS 8-557-5040 703/557-5040

EPISODE NO:	**BATCH NO:**

SCC DIOXIN SHIPMENT RECORD

Site Name:	Sampling Office:	Ship To:
City & State:	City & State:	Date Shipped:
EPA Site No:	Sampling Contact: (name)	
Latitude:	Sampling Date:	
Longitude:		
Tier: 1 2 3 4 5 6 7 (circle one)		

SAMPLE NUMBERS	MATRIX						DESCRIPTION		ADD'L. ANALYSIS
	FISH TISSUE	SEDIMENT	SOIL	WATER	SOLVENT	OTHER:	FIELD SAMPLE	OTHER:	SPECIFY:

WHITE—SCC Copy **GREEN**—Duluth ERL Copy **YELLOW**—Region Copy **PINK**—Lab Copy for Signature & Return to SCC **GOLD**—Lab Copy

Figure 6-10. Dioxin Shipment Record Form

U. S. EPA ECC Toxicant Analysis Center
Building 1105
Bay St. Louis, MO 39529

Attention: Danny McDaniel

Subject: Tier 4 - Analysis Instructions

Dear Sir:

The objective of this letter is to clarify extraction and analysis instructions and priorities for individual samples from specific Tier 4 combustion sites. This instruction letter is # x and pertains to EPA Site #.

The following samples require immediate extraction and analysis:

SCC # Container # Fraction

The various fractions of the Modified Method 5 sampling train and the recovery sequence utilized is indicated in the attached flowchart. In order to reduce the number of samples for analysis, certain fractions of the sample can be combined. If multiple filters with the same SCC# are present, they can be extracted collected. The XAD-2 resin should be extracted and analyzed separately.

The following samples need to be extracted immediately upon receipt and held for later analysis. The goal is to extract these samples within 7 days of sampling.

SCC # Container # Fraction

The following samples should be held for later extraction and analysis pending the results of Priority #1 samples:

SCC # Container # Fraction

If there are any questions concerning this sample shipment, please contact either Bob Jongleux or Larry Keller of Radian Corporation at (919) 541-9100.

Sincerely,

Test Team Leader

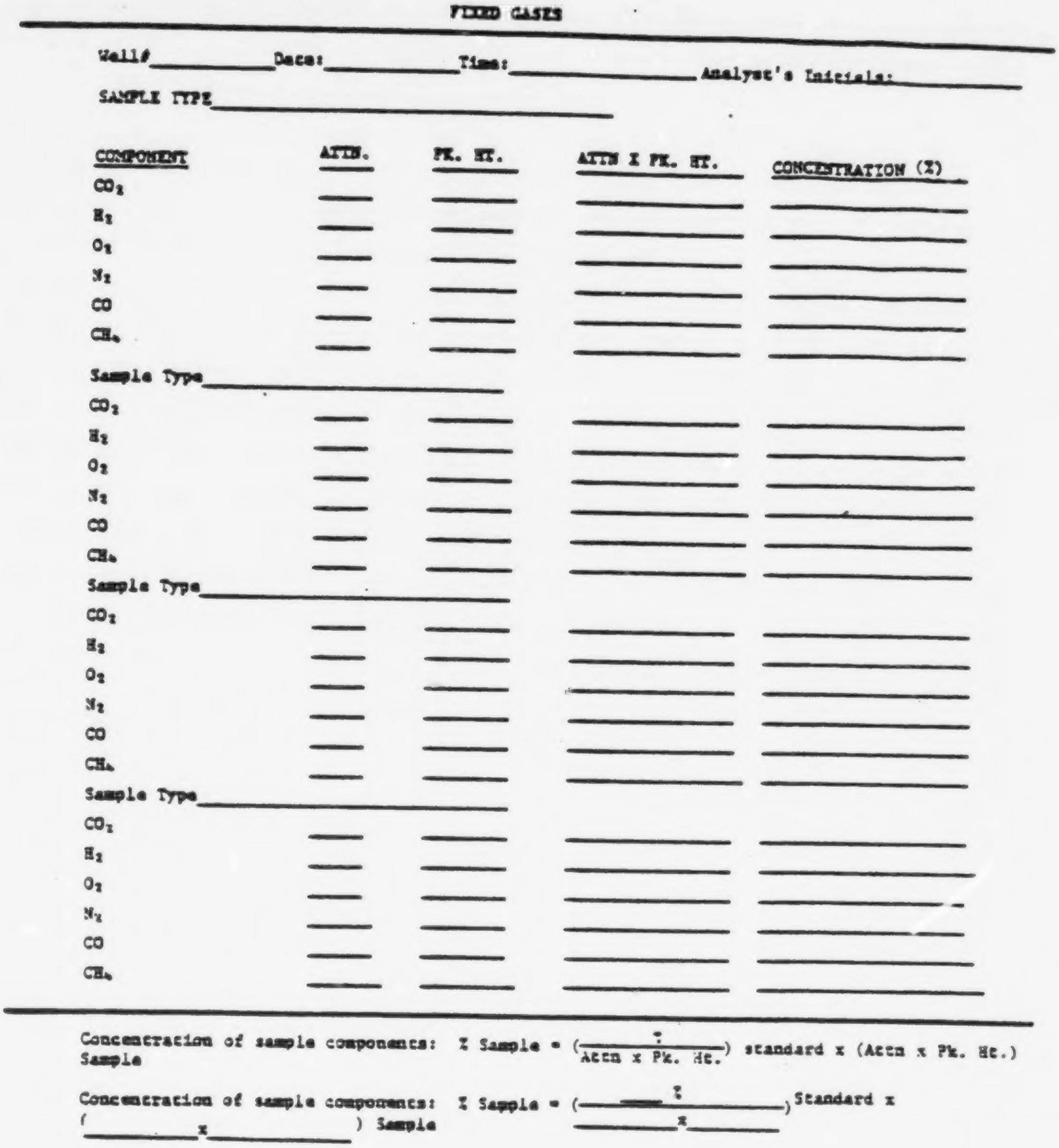
Figure 6-11. Example of Analysis Instructions Letter

record various types of information, such as minor problems which arise, sketches of sampling locations, names and phone numbers of plant contacts, daily activity summaries, etc.

6.2 ANALYTICAL OPERATIONS

Analytical operations will be performed on site in the mobile laboratory as well as in the Radian RTP and Troika laboratories.

The analytical data form to be used for fixed gas (molecular weight) determinations in the field is shown in Figure 6-12. Continuous monitor analyses will utilize Monitor Labs Model 9302 voltage recorder for data acquisition at the first several test sites. For later sites, the continuous monitors will utilize a microprocessor (COMPAQ) data acquisition/reduction system with disk storage capability. An example of the anticipated computer data printout is shown in Figure 6-13. Strip chart recorders will also be used to provide hard copy backup at all test sites. Results from ion chromatograph analyses will be reported on the data forms shown in Figure 6-14. Calibration and QC data for all analytical operations will be recorded in dedicated logbooks and on the QC data summary forms shown in Section 9.0.



FIXED GASES

Well# ________ Date: ________ Time: ____________ Analyst's Initials: ____________

SAMPLE TYPE ______________________________

COMPONENT	ATTN.	PK. HT.	ATTN X PK. HT.	CONCENTRATION (%)
CO_2				
H_2				
O_2				
N_2				
CO				
CH_4				
Sample Type ____________				
CO_2				
H_2				
O_2				
N_2				
CO				
CH_4				
Sample Type ____________				
CO_2				
H_2				
O_2				
N_2				
CO				
CH_4				
Sample Type ____________				
CO_2				
H_2				
O_2				
N_2				
CO				
CH_4				

Concentration of sample components: % Sample = ($\frac{\%}{\text{Attn x Pk. Ht.}}$) standard x (Attn x Pk. Ht.) Sample

Concentration of sample components: % Sample = ($\frac{\%}{\_\_\_\_\_\_ \text{ x } \_\_\_\_\_\_}$) Standard x (________ x ________) Sample

Figure 6-12. Example of Fixed Gases Analytic Data Sheet

```
 TIME         O2        CO        CO2       NOX       THC
             (%V)     (PPMV)      (%V)     (PPMV)    (PPMV)

=======   =======   =======   =======   =======   =======

    945      11.2    1213.2      19.2     677.8      18.9
    950      11.3    1960.8      19.6     768.7      10.8
    955      11.3    1547.9      19.7     695.2       8.6
   1000      11.2    1226.0      18.6     691.9       7.7
   1005      11.3    1788.0      16.2     784.8       7.5
   1010      11.3    1350.5      18.8     787.2       7.2
   1015      11.4    1248.7      15.5     737.7       7.1
   1020      10.9    1375.4      17.2     705.1       6.7
   1025      10.8    1225.7      14.4     708.9       6.6
   1030      11.4    1498.6      16.7     786.0       7.0
   1035      11.2    1400.2      14.5     815.2       9.4
   1040      11.6    1380.5      14.9     739.9       8.7
   1045      12.1    1672.3      21.1     810.0       8.0
   1050      12.4    1744.1      17.2     955.9       7.9
   1055      11.9    1746.2      18.3     806.6       7.5
   1100      12.3    1849.5      22.1     783.1       8.0
   1105      11.8    1381.7      17.4     740.6       9.8
   1110      11.8    1524.1      15.6     808.5       6.8
   1115      11.7    1374.0      17.7     777.4       5.9
   1120      11.8    1490.6      18.9     673.4       6.3
   1125      12.4    2247.7      16.0     930.9       7.0
   1130      11.6    1495.6      15.3     712.3       5.8
   1135      12.4    2230.3      18.4     804.1       6.9
   1140      11.7    1411.7      17.2     857.3       6.4
   1145      12.3    1618.9      18.1     651.5       5.9
   1150      12.5    2598.9      18.1     935.7       7.2
   1155      11.6    1483.9      15.9     740.0       6.4
   1200      12.9    2962.3      17.7     749.9       7.8
   1205      12.2    1708.9      18.5     724.5       7.5
   1210      11.4    1641.4      17.4     725.6       6.0
   1215      11.9    2105.8      16.5     890.2       7.6
   1220      11.8    1951.4      17.9     631.9       5.0
   1225      11.8    1846.5      18.2     792.8       5.9
   1230      11.7    2408.1      14.5     846.6       6.1
   1235      12.0    2045.1      17.5     780.7       6.4
   1240      11.7    2014.4      16.0     748.1       6.0
   1300      11.6    2081.8      16.8     738.7       5.3
   1305      12.0    2366.2      18.2     750.7       5.7
   1310      11.7    2573.3      15.3     767.7       5.7
   1315      11.7    2661.1      16.0     800.0       5.8
   1320      11.9    2295.8      16.9     681.2       5.6
   1325      11.9    2508.1      17.1     725.0       6.6
   1330      11.7    2358.8      19.9     700.3       5.5
   1335      11.8    2824.9      20.5     750.0       5.3
   1340      11.8    2258.2      15.2     713.7       5.4
   1345      11.9    2504.1      18.4     745.2       9.6
   1350      11.6    1904.1      14.6     708.5       5.3
   1355      11.6    1952.9      15.7     728.7       5.0
   1400      11.5    2223.5      17.0     705.8       5.3
   1405      11.3    2777.6      17.4     767.7       5.1
```

FIGURE 6-13. Example of continuous monitor data printout

ION CHROMATOGRAPHY

Sample ID	Bottle Dilution Factor	Dionex Dilution Factor	Peak Height	mmole/ℓ Injected	Total mmole/ℓ	Anion or Retention Time	Operator Initials	Date

Figure 6-14. Ion Chromatagraph Data Sheet

SECTION 7

CALIBRATION PROCEDURES

Information is presented in this section pertaining to the calibration of both sampling and analytical systems. Included is a description of the procedures or reference to applicable standard operating procedures, the frequency, and the calibration standards used.

7.1 SAMPLING EQUIPMENT CALIBRATION PROCEDURES

The checkout and calibration of source sampling equipment is an important function in maintaining data quality. Referenced calibration procedures will be strictly followed when available, and the results properly documented and retained. If a referenced calibration technique for a particular piece of apparatus is not available, then a state-of-the-art technique will be used. A discussion of the techniques used to calibrate this equipment is presented below.

7.1.1 Type-S Pitot Tube Calibration

The EPA has specified guidelines concerning the construction and geometry of an acceptable Type-S pitot tube. If the specified design and construction guidelines are met, a pitot tube coefficient of 0.84 can be used. Information related to the design and construction of the Type-S pitot tube is presented in detail in Section 3.1.1 of EPA document 700/4-77-027b (7). Only Type-S pitot tubes meeting the required EPA specifications will be used during this project. Pitot tubes will be inspected and documented as meeting EPA specifications prior to the field sampling. An example of the pitot inspection form is shown in Figure 7-1.

7.1.2 Sampling Nozzle Calibration

EPA Method 5 prescribes the use of stainless steel buttonhook nozzles for isokinetic particulate sampling. Calculation of the isokinetic sampling rate requires that cross sectional area of the sampling nozzle be accurately

PITOT TUBE INSPECTION FORM

Date: ____________ Operator Initials: ____________

Pitot Tube I.D. No.: ________ Length: ____________

Pitot tube assembly level? ________ yes ________ no

Pitot tube openings damaged? ________ yes (explain below) ______ no

Quick connects attached, leak free? ________ yes ________ no

α_1 = ________° α_2 = ________°

β_1 = ________° β_2 = ________°

γ = ________°, θ = ________°, A = ______ cm (in.)

z = A sin γ = ______ cm (in.);

w = A sin θ = ______ cm (in.);

P_A = ____________ cm (in.);

P_b = ____________ cm (in.);

D_t = ____________ cm (in.)

Acceptance Criteria:

α_1 and α_2 < 10° ________ yes ________ no

β_1 and β_2 < 5° ________ yes ________ no

z < 0.32 cm (1/8 in.) ____ yes ________ no

w < 0.08 cm (1/32 in.) ____ yes ________ no

P_A and P_b, $1.05\ D_t < P < 1.50\ D_t$ ________ yes ________ no

D_t, 0.48 cm (3/16 in) $\leq D_t \leq$ 0.95 cm (3/8 in) ________ yes ______ no

Pitot Tube Acceptable? ________ yes ______ no

Comments: ____

____

____

Figure 7-1. Pitot Tube Inspection Form

and precisely known. All nozzles used for modified Method 5 particulate sampling will be thoroughly cleaned, visually inspected and calibrated according to the procedure outlined in Section 3.4.2 of EPA document 600/4-77-027b.

7.1.3 Temperature Measuring Device Calibration

Accurate temperature measurements are required during source sampling. Bimetallic stem thermometers and thermocouple temperature sensors will be calibrated using the procedure described in Section 3.4.2 of EPA document 600/4-77-027b. Each temperature sensor will be calibrated at a minimum of three points over the anticipated range of use against a NBS-traceable mercury-in-glass thermometer. Table 7-1 summarizes the type of temperature calibrations to be performed and the accepted levels of variance. All sensors will be calibrated prior to field sampling. An example calibration form is shown in Figure 7-2.

7.1.4 Dry Gas Meter Calibration

Dry gas meters (DGMs) will be used in the modified Method 5, Method 5, HCl acid train, and ambient XAD sampling collection system to monitor the sampling rate and to measure the sample volume. All dry gas meters will be calibrated (documented correction factor) just prior to the departure of the equipment to the field. A post test calibration check will be performed as soon as possible after the equipment has returned to RTP. Pre- and post-test calibrations should agree within five percent.

Dry gas meters will be calibrated using the calibration system illustrated in Figure 7-3. Prior to calibration, a positive pressure leak-check of the system will be performed using the procedure outlined in Section 3.3.2 of EPA document 600/4-77-237b. The system is placed under approximately ten inches of water pressure and a gauge oil manometer used to determine if a pressure decrease can be detected over a one-minute period. If leaks are detected, they will be eliminated before actual calibrations are performed.

After the sampling console is assembled and leak-checked, the pump will be allowed to run for 15 minutes. This will allow the pump and dry gas meter to warm up. The valve is then adjusted to obtain the desired flow

TABLE 7-1. SUMMARY OF TEMPERATURE CALIBRATION REQUIREMENTS

Temperature Sensor Usage	Number of Calibrations	Calibration Media Ice Bath (0°C)	Ambient Air (20°C)	Hot Water (40-50°C)	Boiling Water (100°C)	Boiling Oil (150-250°C)	Tolerances
Impinger Thermometer	2	*	*				±1°C
Dry Gas Meter Thermometer	2		*	*			±3°C
Stack Temperature Sensor	3	*			*	*	±1.5% of reference temperature

TEMPERATURE INDICATOR IDENTIFICATION NO. (T_{Test})	NBS THERMOMETER SERIAL NO. (T_{STD})	DATE (MMDDYY)	INITIALS OF CALIBRATOR	CALIBRATION DATA	
				MEASURED T_{Test}	MEASURED T_{STD}

Figure 7-2. Temperature Sensor Calibration Form

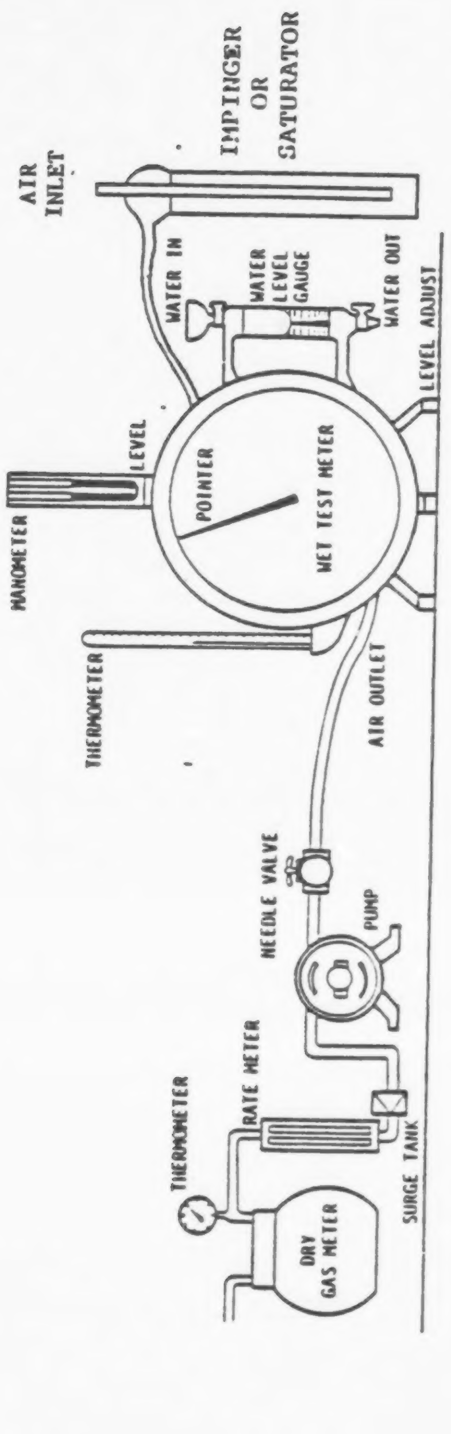

IMPINGER OR SATURATOR
AIR INLET
WATER IN
WATER LEVEL GAUGE
WATER OUT
LEVEL ADJUST
LEVEL
MANOMETER
POINTER
WET TEST METER
THERMOMETER
AIR OUTLET
NEEDLE VALVE
PUMP
RATE METER
THERMOMETER
SURGE TANK
DRY GAS METER

Figure 7-3. DGM Calibration System

rate. After ten minutes, the valve is closed and a final set of data are recorded. A duplicate calibration at the same flow rate is then performed. Additional calibrations are performed if necessary until the calibration results (Y_1) vary by no more than two percent. The average Y_1 is then calculated and recorded on the face of the DGM console. An example DGM calibration data form is presented in Figure 7-4.

Rockwell Model 175 dry gas meters will be used during this project. DGM calibrations will be performed at Radian's RTP, N.C. laboratory using an American Wet Test Meter as an intermediate standard. The "intermediate standard" is calibrated every 6 months against the EPA wet test meter at EPA's Emissions Measurement Laboratory in Research Triangle Park, NC.

7.2 ANALYTICAL CALIBRATION PROCEDURES

Instrument calibrations will consist of calibrations for the continuous monitors to be used for measuring CO, CO_2, O_2, NO_X, SO_2, and THC, the GC/MS for quantitation of polychlorinated biphenyls (PCB), chlorobenzenes (CB) and chlorophenols (CP) in process samples, the ion-chromatograph for measuring total chloride in HCl acid train impinger catches, and the GC/TCD for molecular weight determinations. The standards which will be used for the continuous monitors are presented in Table 7-2. Calibration requirements are summarized in Table 7-3.

7.2.1 Continuous Monitors

Calibrations of all continuous monitors, with the exception of the THC analyzer, will be accomplished by introducing standard gases at the inlet of the gas sample conditioner. Standards for the THC analyzer will be introduced directly into the instrument. Prior to testing at each site, zero nitrogen will be introduced upstream of the sample acquisition system to provide a leak check and a system blank for THC. The acceptance criteria for the THC system blank is 5 ppmv or 1 percent of the span value, whichever is smaller. If this criteria is not met, the sampling system will be cleaned and the system blank repeated. The acceptance criteria for the leak check with zero nitrogen will be a measurement of less than 0.5 percent O_2 at the Beckman oxygen analyzer after calibration.

METER BOX CALIBRATION DATA AND CALCULATION FORM

(English units)

Date ____________________ Meter box number ________________

Barometric pressure, P_b = ________ in. Hg Calibrated by __________________

Orifice manometer setting (ΔH), in. H_2O	Gas volume		Temperatures				Time (θ), min	Y_i	$\Delta H@_i$ in. H_2O
	Wet test meter (V_w), ft^3	Dry gas meter (V_d), ft^3	Wet test meter (t_w), °F	Dry gas meter					
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Avg[a] (t_d), °F			
0.5	5								
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
							Avg		

ΔH, in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w\ P_b(t_d + 460)}{V_d(P_b + \frac{\Delta H}{13.6})\ (t_w + 460)}$	$\Delta H@_i = \frac{0.0317\ \Delta H}{P_b\ (t_d + 460)} \left[\frac{(t_w + 460)\ \theta}{V_w}\right]^2$
0.5	0.0368		
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

Figure 7-4. Dry gas meter calibration form.

TABLE 7-2. STANDARDS FOR CONTINUOUS MONITOR

Analytical Parameter	Standard	Source	Documentation
$CO/CO_2/O_2$ Quantitation	CO - 5,400 ppmv, CO_2 - 18% O_2 - 22%, N_2 - Bal.; CO - 500 ppmv, CO_2 - 5%, O_2 - 3%, N_2 - Bal.; CO - 2,700 ppmv, N_2 - Bal.; CO - 2,000 ppmv, CO_2 - 12% O_2 - 9%, N_2 - Bal.	Airco	Certified[a]
NO_x Quantitation	NO - 20 ppmv, N_2 - Bal.; NO - 90 ppmv, N_2 - Bal.; NO - 150 ppmv, N_2 - Bal.; NO - 1,000 ppmv, N_2 - Bal.	Airco	Certified[a]
SO_2 Quantitation	SO_2 - 90 ppmv, N_2 - Bal.; SO_2 - 405 ppmv, N_2 - Bal.; SO_2 - 1,000 ppmv, N_2 - Bal.	Airco	Certified[a]
THC Quantitation	Propane-20 ppmv, Air-Bal.; Propane-60 ppmv, Air-Bal.; Propane-90 ppmv, Air-Bal.; Propane-300 ppmv, Air-Bal.; Propane-800 ppmv, Air-Bal.	Airco	Certified[a]

[a] "Certified" standards are mixtures analyzed by the gas manufacturer, with the analytical accuracy certified to be ±2 percent. Analyses are referenced to NBS standard reference materials if SRMS exist or to gravimetric standards, which are gravimetrically traceable to NBS.

TABLE 7-3. SUMMARY OF ANALYTICAL CALIBRATION REQUIREMENTS

Parameter	Method of Analysis	Type of Calibration	Calibration Standards	Frequency	Acceptance Criteria
CO/CO$_2$	Anarad 412 (NDIR)	Multipoint (Zero plus 2 upscale)	CO and CO$_2$ in N$_2$	Once per site prior to testing	Correlation coefficient $\geq$ 9950
		Single point RF	CO and CO$_2$ in N$_2$	Daily (prior to testing)	Agreement within 20% of multipoint RF
		Analytical Blank	Zero N$_2$	Daily (prior to testing)	Zero value $\leq$1% of span
		Single point drift check	CO and CO$_2$ in N$_2$	Daily (at conclusion of analysis)	RF agreement within 10% of RF for single point RF check
O$_2$	Beckman 755 (Paramagnetic)	Same as CO/CO$_2$	O$_2$ in N$_2$	Same as CO/CO$_2$	Same as CO/CO$_2$
THC	Beckman 402 (Flame ionization analyzer)	Same as CO/CO$_2$	Propane in air	Same as CO/CO$_2$	Same as CO/CO$_2$ except zero value of $\leq$5ppmv or 1% of span whichever is smaller.
NO$_x$	Teco 10AR (Chemiluminescence)	Same as CO/CO$_2$	NO in N$_2$	Same as CO/CO$_2$	Same as CO/CO$_2$
SO$_2$	Teco 40 (Pulsed Fluorescent)	Same as CO/CO$_2$	SO$_2$ in N$_2$	Same as CO/CO$_2$	Same as CO/CO$_2$
Polychlorinated biphenyls (PCB)	GC/MS	Multipoint (zero plus 4 upscale)	PCB's	Once (prior to analyses for PCB)	Correlation coefficient of $\geq$0.90
		Single point check	PCB's	Daily (prior to analyses)	Response within ±15 percent of value predicted from multipoint calibration curve
Chlorobenzenes	GC/MS	Same as PCB	Chlorobenzenes	Same as PCB	Same as PCB
Chlorophenols	GC/MS	Same as PCB	Chlorophenols	Same as PCB	Same as PCB
HCL Acid Train and Process Sample Chlorides	Ion Chromatograph	Multipoint (3 concentrations minimum)	NaCl in H$_2$O	Twice (prior to and upon completion of analyses)	Correlation efficienct $\geq$0.9950 and slope within 10% of running mean for previous six determinations.
HCL Acid Train Sulfates	Ion Chromatograph	Same as Chlorides	NaSO$_4$ in H$_2$O	Same as Chlorides	Same as Chlorides
HCL Acid Train Sodium Ion	Atomic Absorption	Same as Chlorides	NaCl in H$_2$O	Same as Chlorides	Same as Chlorides
Molecular Weight (CO, CO$_2$, O$_2$, N$_2$)	Shimadzu 3BT (GC/TCD)	Single point	CO, CO$_2$, and O$_2$ in N$_2$	Twice (prior to and upon completion of analyses)	Agreement of duplicate analyses within 5 percent (CV).

All instruments will undergo multipoint linearity checks (two points plus zero) bracketing the predicted sample values. These checks will be performed prior to testing at each site or on a weekly basis. In all cases, the acceptance criteria for the linearity checks will be a correlation coefficient of $r \geq 0.9950$. If this criterion is not met, the linearity check will be repeated (following instrument maintenance if judged necessary) until $r \geq 0.9950$ is achieved.

For all continuous monitors, an analytical blank and a single point response factor (RF) standard will be analyzed daily prior to testing. The acceptance criteria for the single point RF will be an RF agreement within 20 percent of the previous multipoint RF. If this criteria is not met, the single point RF check will be repeated. The acceptance criteria for the analytical blank will be ≤1 percent of the instrument span (or ≤5 ppmv for the THC analyzer).

At the end of each day of testing, a single point drift check will be performed by analyzing the same standard used for the single point RF determination. The acceptance criteria for this analysis will be agreement within 10 percent of the single point RF determination. If this criteria is not met, the end of testing RF and the initial single point RF will be used to quantitate samples assuming a linear drift throughout the test day.

7.2.2 GC/MS Calibrations

GC/MS analysis will be used to identify and quantify dioxin precursors (chlorobenzenes, chlorophenols, and polychlorinated byphenyls) present in process and combustion air (ambient XAD) samples. The methods to be used for identification and quantitation of the precursors are discussed below.

7.2.2.1 Qualitative Identification. The identification of the compounds will be based both on the chromatographic elution of those compounds and on the specificity of the detection system. The relative retention time compared to an appropriate internal standard is generally constant to within about ± 0.2 percent, depending upon the compound. For GC/MS, a match in both the relative retention time and the simultaneous elution of multiple analytical ions specific to a compound will serve to establish the qualitative identification of the components of the sample.

For directed analyses, the identification criteria to confirm the presence of the spiked compounds by MS are that the GC retention time for the suspect peak, relative to some standard, match that for the corresponding compound and that the characteristic ions of the compound are present in the unknown sample at approximately the same ratio as is present in the standard and that those ions coelute.

The NBS data base will be used for the computerized mass spectral search. The computerized mass spectral search system will assess the confidence to be placed in a qualitative compound identification or "match" with the reference spectrum in the library. The computerized search system typically generates one or more numerical indicators of the "goodness of fit." In the Finnigan 4023/Incos data system, goodness of fit is indicated by three values:

- the fit - how well each library entry is represented in the sample spectrum;
- the purity - how well the sample spectrum is represented in each library entry; and
- the reverse fit - how well both the fit and the purity match the sample spectrum and the library entry. Complements mainly fit by detecting unknown compounds that may be components of mixtures in the library or structurally related to substructures of the library.

Of these terms, the purity is the most powerful since a high purity value indicates that both the library entry and the sample spectrum match each other closely and either spectrum accounts for virtually all of the other spectrum. Qualitative compound identification of the compounds will be based on the purity value. For purity values in excess of 900 on the 1 to 999 scale, the computer search could be regarded as having identified a single component in the GC peak. A list of the top 5 choices will also be retrieved as output from the search system. If several compounds are identified with purity values that are close to one another, the analyst will retrieve and examine the library spectra and use the elution order data to ascertain the best candidate for the identity of the GC peak of interest.

Similarly, if the purity value has decreased below the 900 value threshold, the analyst will retrieve and examine the library spectra, the sample spectrum, and any retention time data to determine the identification of the sample compound.

All compound identifications will be reported with an indication of the goodness of fit criteria that were used in making the assignment. This may include numerical values of parameters from the computerized search system and/or the analyst's professional judgment (e.g., "strong," "probable," "tentative"). Elution order, retention time, and accordance with the reference spectrum will be utilized to assure correct identification.

7.2.2.2 Quantitation. The quantity of dioxin precursors present in a sample will be determined using an "internal standard" calibration procedure. The compounds of interest will be calibrated against a fixed concentration of a noninterfering internal standard selected to be representative of the compound type being quantitated. A response factor calibration curve for the compounds relative to the internal standard will be developed based on a multipoint calibration with nominal compound levels ranging from 1 to 100 µg/ml. Immediately prior to analysis, each sample will be spiked with a known amount of the internal standard. Compounds of interest in the sample will then be quantitated by comparing the relative response of the compound and internal standard against the response factor calibration curve. Calibration standards for the GC/MS analysis will be prepared from stock standards by dilution of aliquots with the appropriate solvent.

The multipoint calibration and linearity check (zero plus four up-scale points) will be performed prior to the start of analysis for each precursor class. The calibration concentrations will bracket the expected working range of the sample concentrations and will include at least one concentration near, but above, the minimum detection limit (MDL). At the start of each subsequent analysis day, a single point calibration check will be performed. The acceptance criterion for the linearity check will be a correlation coefficient of $r \geq 0.90$. If this criterion is not met, additional calibration points will be run or several points will be repeated until r ≥0.90 is achieved. The acceptance criteria for the daily single point RF check will be a response within ± 15 percent of the response predicted by the multipoint calibration curve. If this criteria is not met, the single point RF check will be repeated with a fresh calibration standard or the multipoint calibration will be repeated.

7.2.3 Ion Chromatograph and Atomic Absorption Spectrometer Calibration

The ion chromatograph and atomic absorption spectrometer will be calibrated twice for each sample set analyzed. One calibration will be performed prior to sample analyses and a second will be performed after all sample analyses are completed. This will be accomplished by introducing different standard solutions into the instrument. A minimum of three concentrations will be used to generate a calibration curve. The calibration curve will be considered acceptable if the correlation coefficient is greater than 0.9950, and if the slope is within 10 percent of the running mean for the previous six determinations.

7.2.4 Analytical Balance Calibration

Analytical balances will be calibrated over the expected range of use with standard weights (NBS Class S). Measured values must agree within ±0.1 mg. The balances will be calibrated prior to the field measurement program.

Field checks of balance accuracy will be made monthly using a set of weights which have previously been weighted side-by-side with the NBS traceable weights. The balance calibration data sheet is illustrated in Figure 7-5.

7.2.5 Molecular Weight Calibrations

The Shimadzu 3BT analyzer to be used for molecular weight determinations will be calibrated with one or more standards containing appropriate concentrations of CO, CO_2, O_2, and N_2. The calibration gas(es) will be run immediately before and after sample analysis. Analysis of the calibration gas(es) will be repeated until two consecutive analyses are obtained which agree within ± 5 percent. This same acceptance criteria of ± 5 percent for duplicate analyses will be required during the sample quantitation.

ANALYTICAL BALANCE FORM

MODEL____________________ IDENTIFICATION NO.____________________

CLASSIFICATION OF STANDARD WEIGHTS____________________

	0.5000 g	1.0000 g	10.0000 g	50.0000 g	100.000 g
Date					
Analyst					
Measured Weight					
Reference Weight					
Deviation					
% Deviation* (from Reference Weight)					
Date					
Analyst					
Measured Weight					
Reference Weight					
Deviation					
% Deviation* (from Reference Weight)					

$$* \text{ Deviation} = \frac{\text{Deviation}}{\text{Reference Weight}} \times 100\%$$

Figure 7-5. Balance calibration data sheet.

SECTION 8

DATA REDUCTION, VALIDATION, AND REPORTING

8.1 RESPONSIBILITIES

Table 8-1 contains a list of data reduction, data validation, and reporting tasks along with the person(s) responsible for each task. Also included in Table 8-1 are those person(s) responsible for data review. Those who have been identified previously as task leaders will have primary responsibility for their tasks as listed in Table 8-1.

8.2 DATA REDUCTION

Many calculations from raw data are included on the field data sheets and these are not repeated here. Calculations not yet presented are addressed below.

8.2.1 Velocity and Volumetric Flow Rate

Velocity and temperature profile data are used in conjunction with the gas composition data (moisture and fixed gases) to calculate the process gas velocity and volumetric flow rate. An example calculation worksheet for these parameters is presented as Figure 8-1.

8.2.2 Moisture Content

Dry gas meters will be used to measure the volume of gas samples for Method 4. The calculations required to convert metered gas volumes to standard gas volumes are presented below.

$$V_{m(std)} = 17.64 \frac{(V_m)(DGMCF)(P_m)}{T_m} \qquad (8\text{-}1)$$

TABLE 8-1. SUMMARY OF DATA REDUCTION, REVIEW AND VALIDATION, AND REPORTING RESPONSIBILITIES

	Personnel Responsibilities		
Task	Data Reduction	Data Review & Validation	Reporting
Site-Specific Test Plans			L. E. Keller M. A. Palazzolo
Quality Assurance Project Plan		D. L. Lewis	M. A. Palazzolo
Site-Specific Data Summaries	Field Team Members	R. F. Jongleux J. R. McReynolds	R. F. Jongluex J. R. McReynolds
QC Data Summaries	Field Team Members	D. L. Lewis	M. A. Palazzolo L. E. Keller
QA Audit Report			D. L. Lewis
QC Reports (Input to Interim Reports)			D. L. Lewis
Site-Specific Test Reports		A. J. Miles	L. E. Keller M. A. Palazzolo
Final Report Outline		R. M. Parks	A. J. Miles
Draft Final Report		R. M. Parks	A. J. Miles
Final Report		R. M. Parks	A. J. Miles

VELOCITY AND VOLUMETRIC FLOW RATE CALCULATIONS WORKSHEET

Input: Pitot ΔP (ΔP, in. H_2O); stack temperature (T_s, °R); wet molecular weight of gas (M_s), from gas analysis; absolute stack pressure (P_s, in. Hg); pitot tube correction factor (PTCF), usually 0.84; moisture fraction (B_{ws}); cross-sectional area of stack or duct (A), ft^2.

Preliminary Calculations:

1) Average $\sqrt{\Delta P} = \frac{\Sigma\sqrt{\Delta P}}{N} = \underline{\hspace{6cm}}$

Where N is the number of points measured. For one point, just use $\sqrt{\Delta P}$.

2) Wet molecular weight (M_s) (e.g., using Orsat and EPA Method 4 data), g/g-mole

$$M_s = [44(\text{Dry } \%CO_2) + 32(\text{Dry } \%O_2) + 28(\text{Dry } \%CO) + 28(\text{Dry } \%N_2)] \times (.01)$$
$$\times\ (\text{1-Moisture Fraction}) + 18(\text{Moisture Fraction})$$
$$= [44 \times \underline{\hspace{1.5cm}} + 32 \times \underline{\hspace{1.5cm}} + 28 \times \underline{\hspace{1.5cm}} + 28 \times \underline{\hspace{1.5cm}}] \times (.01)(1-B_{ws}) + 18(B_{ws})$$
$$= \underline{\hspace{5cm}}\text{g/g-mole}$$

3) Absolute Stack Pressure (P_s), "Hg

$$P_s = (\text{Barometric Pressure, "Hg}) + (\text{Stack Static Pressure, "}H_2O)\ (.07355)$$
$$= (\underline{\hspace{2cm}}\text{ "Hg}) + (\text{Stack Static Pressure, "}H_2O)\ (0.07355)$$
$$= \underline{\hspace{2cm}}\text{ "Hg}$$

4) Absolute Stack Temperature (T_s), °R

$$T_s = (\text{Stack Temperature, °F}) + 460$$
$$= (\underline{\hspace{2cm}}\text{°F}) + 460$$
$$= \underline{\hspace{2cm}}\text{°R}$$

Final Calculations:

5) Average stack gas velocity (V_s), ft/sec

$$V_s = (85.49)(\text{PTCF})\sqrt{\frac{T_s}{(M_s)(P_s)}}\quad(\text{Ave }\sqrt{\Delta P})$$
$$V_s = (85.49)(\underline{\hspace{1cm}})\sqrt{\frac{(\underline{\hspace{1cm}}\text{°R})}{(\underline{\hspace{1cm}}\text{g/g-mole})(\underline{\hspace{1cm}}\text{"Hg})}}\quad(\underline{\hspace{1cm}})$$
$$V_s = \underline{\hspace{2cm}}\text{ft/sec}$$

6) Volumetric flow rate, dry, standard conditions (Q_{sd})

$$Q_{sd} = 60(1-B_{ws})(V_s)(A)\left(\frac{T_{std}}{T_{s(ave)}}\right)\left(\frac{P_s}{P_{std}}\right)$$
$$Q_{sd} = 60(1-\underline{\hspace{1cm}})(\underline{\hspace{1cm}})(\underline{\hspace{1cm}})\left(\frac{528\text{°R}}{\underline{\hspace{0.8cm}}\text{°R}}\right)\left(\frac{\underline{\hspace{1cm}}\text{"Hg}}{29.92\text{"Hg}}\right)$$
$$Q_{sd} = \underline{\hspace{1.5cm}}\text{ft}^3\text{/min, dry, standard conditions}$$

Run#__________ Date__________ Time__________ Signature______________________________

FIGURE 8-1. Velocity and volumetric flow rate calculations worksheet.

Based on the weight gain of the impingers, the volume of water vapor collected, at standard conditions (68°F and 29.92 inches of mercury), is calculated as follows:

$$V_{w(std)} = 0.0472\ (W_f - W_i) \qquad (8\text{-}2)$$

Finally, the moisture content (i.e., moisture fraction) of the gas stream is calculated as:

$$B_{ws} = \text{Moisture Fraction} = \frac{V_{w(std)}}{V_{w(std)} + V_{m(std)}}$$

Nonmenclature

B_{ws} = moisture fraction

DGMCG = dry gas meter correction factor

P_m = meter pressure (barometric pressure), in. Hg

T_m = average meter temperature, °R (°F + 460)

V_f = final meter volume, ft^3

V_i = Initial meter volume, ft^3

V_m = metered gas volume, ft^3 = $(V_f - V_i)$(DGMCF)

$V_{m(std)}$ = metered gas volume, standard temperature and pressure (STP), ft^3

$V_{w(std)}$ = volume of water vapor collected, STP, ft^3

W_f = final weight of impingers, g

W_i = initial weight of impingers, g

8.2.3 HCL Concentration

HCL concentration in the flue gas, based on ion chromatography will be calculated for most combustion sources as:

$$C_{HCL} = \frac{(8.04 \times 10^{-8})\ (IC_{CL})\ (V_{Soln})}{Vm\ (std)}$$

For flue gases from black liquor recovery boilers, HCL concentrations in the flue gas will be calculated as:

$$C_{HCL} = \frac{(8.04 \times 10^{-8})\ [IC_{CL} - IC_{Na} + 2(AA_{SO_4})]\ (V_{Soln})}{Vm\ (std)}$$

Nonmenclature

C_{HCL} = concentration of HCL, dry basis corrected to standard conditions, lb/dscf

V_{soln} = total volume of solution in which HCL is contained, mℓ

IC_{CL} = blank corrected sample Cl^- concentration as measured by ion chromatagraphy, mM/ℓ

IC_{Na} = blank corrected Na^+ concentration as measured by ion chromatography, mM/ℓ

AA_{SO4} = blank corrected SO_4^{--} concentration as measured by atomic absorption spectroscopy, mM/ℓ

8.04×10^{-5} = conversion factor

8.2.4 Total Particulate Mass Concentration

Total particulate mass concentration is calculated based on the total mass of particulate collected, including filter catch and acetone rinse, and the sample gas volume, as:

$$C_s = (0.001\ g/mg)\ \frac{M_n}{V_{m(std)}} \quad (15.43)$$

Nonmenclature

C_s = concentration of particulate matter in flue gas, dry basis corrected to standard conditions, gr/dscf

M_n = total amount of particulate matter collected, mg

$V_{m(std)}$ = dry gas volume, corrected to standard conditions, dscf

15.43 = conversion factor, gr/g

8.2.5 Dioxin Mass Concentration

The flue gas concentration of dioxin will be calculated from the modified Method 5 train results as follows:

$$C_{Dioxin} = \frac{(2.203 \times 10^{-9})\ M_{mm5} - M_B}{Vm\ (std)} \qquad (8\text{-}6)$$

Nonmenclature

C_{Dioxin} = concentration of dioxin, dry basis corrected to standard conditions, lb/dscf

M_{mm5} = total mass of dioxin or any given dioxin isomer in the modified Method 5 sample train as determined by the GC/MS analysis done by Troika, ng

M_B = mass of dioxin or dioxin isomer in modified Method 5 blank as determined by Troika, ng

(2.203×10^{-9}) = conversion factor

8.2.6 Continuous Monitors

Response factors (RF) for the continuous monitors will be calculated from the single point RF check and the instrument zero value as follows:

$$RF = \frac{Cstd}{[(\%FS)std - (\%FS)zero]} \qquad (8\text{-}7)$$

Using this response factor, the sample concentrations will be calculated using the following equations:

$$C_{smpl} = [(\%FS)_{smpl} - (\%FS)_{zero}] \times RF \qquad (8\text{-}8)$$

Nonmenclature

RF = response factor or calibration factor for the parameter calibrated, CO, CO_2, O_2, NO_x, SO_2, or THC

C_{std} = certified concentration of the parameter in the calibration gas

$(\% FS)_{std}$ = calibration standard response expressed as percent of full-scale output (on strip chart recorder or instrument output voltage).

$(\% FS)_{zero}$ = zero standard response expressed as percent of full-scale

$(\% FS)_{smpl}$ = sample response expressed as percent of full-scale output

Measurement of sample SO_2 concentrations using the Teco Model 40 pulsed fluorescent analyzer will require a correction for the quenching effect of O_2 and CO_2 in the flue gas sample compared to the calibration standard. Quenching coefficients for O_2 and CO_2 relative to N_2 have been determined by the instrument manufacturer (1). The correction factor (K_f) for given flue gas O_2 and CO_2 concentrations can be calculated as follows, provided that the SO_2 standards used for calibration are in NO_2 with no O_2 or CO_2:

$$K_f = 1 + 0.02139\ (\% O_2) + 0.01436\ (\% CO_2) \qquad (8\text{-}9)$$

Using this correction, the actual sample concentration is:

$$C_{SO_2} = K_f\ C_{smpl} \qquad (8\text{-}10)$$

where C_{smpl} is calculated according to Equation 8-8.

8.2.7 GC/MS Analysis

The GC/MS will be used to measure precursor concentrations in the process samples and the ambient XAD samples. Single point response factors for the compounds of interest relative to the internal standards will be calculated as follows:

$$RRF_i = \frac{A_s\ C_{is}}{A_{is}\ C_s} \qquad (8\text{-}11)$$

For the sample quantitation, an average response factor will be calculated from all previous single point calibrations using the equation:

$$RRF_s = \frac{\Sigma RRF_i}{N} \qquad (8\text{-}12)$$

The concentration of a given compound in the sample will then be calculated as follows:

$$C_{unk} = \frac{C_{is}}{A_{is}} \times \frac{A_{unk}}{RRF_s} \qquad (8\text{-}13)$$

Nomenclature

RRF_i = relative response factor for compound of interest and internal standard, single point calibration

RRF_s = average relative response factor

A_s = area of the characteristic ion for the compound of interest

A_{is} = area of the characteristic ion for the internal standard

C_{is} = concentration of internal standard (μg/ml)

C_s = concentration of compound of interest (μg/ml)

C_{unk} = Unknown concentration of compound in sample (μg/ml)

A_{unk} = area of compound of interest in sample

N = Number of single point calibrations

8.3 DATA VALIDATION

All measurement data will be validated based upon representative process conditions during sampling or testing, acceptable sample collection/testing procedures, consistency with expected and/or other results, adherence to prescribed QC procedures, and the specific acceptance criteria outlined in Section 7 for calibration procedures and in Section 9 for internal quality control procedures. Any suspect data will be flagged and identified with respect to the nature of the problem with validity. Suspected outliers will be tested using the Dixon Criteria at the five percent significance level.

Several of the data validation acceptance criteria presented in Sections 7 and 9 involve specific calculations. Representative examples of these are presented below.

8.3.1 Instrument Response Linearity

Acceptance criteria for instrument response linearity checks are based upon the correlation coefficient, r, of the best fit line for the calibration data points. The correlation coefficient reflects the linearity of response to the calibration gas mixtures and is calculated as:

$$r = \frac{n(\Sigma xy) - (\Sigma x)\ (\Sigma y)}{\sqrt{[n(\Sigma x^2) - (\Sigma x)^2]\ [n(\Sigma y^2) - (\Sigma y)^2]}} \qquad (8\text{-}18)$$

where: x = calibration concentrations
y = instrument response (peak area)
n = number of calibration points (x,y data pairs)

8.3.2 Precision

Control limits for control sample analyses, acceptability limits for replicate analyses, and response factor agreement criteria specified in Sections 7 and 9 are based upon precision, in terms of the coefficient of variation (CV), i.e., the relative standard deviation. The standard deviation of a sample set is calculated as:

$$S = \text{standard deviation} = \sqrt{\frac{\Sigma(x-x)^2}{n-1}} \qquad (8\text{-}19)$$

where: x = individual measurement

$\bar{x}$ = mean value for the individual measurements

n = number of measurements

The CV in percent is then calculated as:

$$CV = \frac{S}{\bar{x}} \times 100\% \qquad (8\text{-}20)$$

Pooled or "average" measurements of CV are calculated as:

$$\text{Pooled CV} = \sqrt{\frac{\sum_{i=1}^{K} CV_i \; Df_i}{\sum_{i=1}^{n} Df_i}} \qquad (8\text{-}21)$$

where: CV_i = CV of data set i

DF_i = degrees of freedom for data set i

K = total number of data sets

i = data set 1, 2, 3, ... K

8.4 REPORTING

Reporting responsibilities for this project are outlined in Table 8-1. These include both formal reports (e.g., QA Project Plan, test plans, final report, etc.) and internal reports (e.g., site-specific data volumes, QC data summaries, etc.).

Upon completion of testing at each site, a site-specific test report will be prepared by the field team leader responsible for that particular test (either Mr. M. A. Palazzolo or Mr. L. E. Keller). The team leader will also be responsible for providing Mr. D. L. Lewis, the QA Coordinator, with completed copies of the QC data forms (Figure 9-1) and a letter status report summarizing the tests conducted and information pertaining to corrective action, calibration data, etc. Mr. Lewis will review and tabulate the QC data and provide data quality input for the site-specific test report.

Following the performance and systems audits, Mr. Lewis will prepare an audit report(s) which details the audit activities, results, and recommendations for corrective action.

As indicated in Table 8-1, Mr. M. A. Palazzolo and Mr. L. E. Keller will be responsible for preparation of the site-specific test plans for each test site. They will be assisted in this effort by Mr. Bob Jongleux and Jim McReynolds. These documents will be based upon information gathered in pre-test surveys.

Mr. A. J. Miles, the Project Director will be responsible for preparation of the final report. Input to this document will be provided by the Task Leaders and other project team members as required.

The reporting schedule is shown as part of the overall schedule of project activities in Figure 1-1.

SECTION 9

INTERNAL QUALITY CONTROL CHECKS

Specific QC procedures will be followed to ensure the continuous production of useful and valid data throughout the course of the Tier 4 test program. The QC checks and procedures described in this section represent an integral part of the overall sampling and analytical scheme. Strict adherence to prescribed procedures is quite often the most applicable QC check. A discussion of both the sampling and analytical QC checks that will be utilized during this program is presented below.

9.1 SAMPLING QUALITY CONTROL PROCEDURES

Prior to actual sampling on site, all of the applicable sampling equipment will be thoroughly checked to ensure that each component is clean and operable. Each of the equipment calibration data forms will be reviewed for completeness and adequacy to ensure the acceptability of the equipment. Each component of the various sampling systems will be carefully packaged for shipment. Upon arrival on site, the equipment will be unloaded, inspected for possible damage and then assembled for use.

The following QC checks are applicable to each of the EPA Methods 2, 3, 4, 5, the Modified 5, the HCL acid train and the ambient XAD:

- Each sampling train will be visually inspected for proper assembly before every use.
- All sampling data will be recorded on standard data forms which will serve as pretest checklists.
- The oil manometer or Magnehelic® gauge used to indicate the differential pressure (ΔP) across the S-type pitot tube will be leveled and zeroed.

- The number and location of the sampling traverse points will be checked before taking measurements.
- The temperature measurement system will be visually checked for damage and operability by measuring the ambient temperature prior to each traverse.
- Duplicate readings of temperature and differential pressure will be taken at each traverse point.
- All sampling data and calculations will be recorded on preformated data sheets.

In addition to the general QC procedures listed above, QC procedures specific to each sampling method will also be incorporated into the sampling scheme. These method specific procedures are discussed below.

9.1.1 Sampling Quality Control Procedures for Modified Method 5

Samples for dioxin analysis will be collected according to the October 1984 version of ASME modified Method 5 protocol. Quality control for this sampling will focus on the following:

- Prior to sampling, each filter will be placed in a labeled individual precleaned glass petri dish.
- All cleaned glassware and prepared sorbent traps will be kept closed with ground glass caps or precleaned foil until assembly of the sample train in the field. The sorbent traps will be immediately recapped when the train is disassembled.
- Assembly and recovery of the MM5 sample trains will be performed in an environment free from uncontrolled dust.
- Sample train blanks will be collected for dioxin analysis.
- Prior to sampling, calcuations will be made to determine the proper size nozzle required to attain isokinetic sampling.
- The sampling nozzle will be visually inspected before and after each run for damage.
- The S-type pitot tube will be visually inspected before and after each run for damage.
- Each leg of the S-type pitot tube will be leak-checked before and after each run.

- The oil manometer or Magnehelic® gauge used to indicate the differential pressure (ΔP) across the S-type pitot tube will be leveled and zeroed.
- The number and location of the sampling points will be checked before taking measurements.
- The temperature measurement system will be visually checked for damage and operability.
- During sampling the roll and pitch axis of the S-type pitot tube and the sampling nozzle will be properly maintained.
- The entire sampling train will be leak-checked before and after each run. If the sampling train is moved from one sampling port to another during a run or the filter is changed, the train will be leak-checked before and after the move or filter change.
- Additional leak checks will be performed if the sampling time must exceed 4 hours.
- The filter and sorbent trap will be maintained at the proper temperature throughout the test run.
- Ice will be maintained in the ice bath throughout each run.
- Dry gas meter readings, ΔP and ΔH readings, temperature readings, and pump vacuum readings will be properly made during sampling at each traverse point.
- Isokinetic sampling will be maintained within ±10 percent.

9.1.2 Quality Control Procedures for Particulate Mass Determination

Total particulate mass concentration in the flue gas will be determined using EPA Method 5. Quality control for Method 5 will focus upon the following procedures:

- Prior to sampling, each glass fiber filter will be equilibrated in a desiccator, weighed to determine its initial mass using an analytical balance, and then each filter will be packaged in labeled, individual glass petri dishes.
- Prior to sampling, calculations will be made to determine the proper size nozzle required to attain isokinetic sampling.

- The sampling nozzle will be visually inspected before and after each run for damage.
- The S-type pitot tube will be visually inspected before and after each run for damage.
- Each leg of the S-type pitot tube will be leak-checked before and after each run.
- The oil manometer or Magnehelic® gauge used to indicate the differential pressure (ΔP) across the S-type pitot tube will be leveled and zeroed.
- The number and location of the sampling points will be checked before taking measurements.
- The temperature measurements system will be visually checked for damage and operability.
- During sampling the roll and pitch axis of the S-type pitot tube and the sampling nozzle will be properly maintained.
- Handling of the filters will be performed in clean areas out of drafts. Teflon®-coated tweezers will be used to transfer the filters at all times.
- The entire sampling train will be leak-checked before and after each run. If the sampling train is moved from one sampling port to another during a run, the train will be leak-checked before and after the move.
- Ice will be maintained in the ice bath throughout each run.
- Dry gas meter readings, ΔP and ΔH readings, temperature readings, and pump vacuum readings will be properly made during sampling at each traverse point.
- Isokinetic sampling will be maintained within ±10 percent.
- In weighing the filters both prior to and after sampling, repeat weighings will be performed ≥ 6 hours after the initial weighings. Repeat weighings must agree within ±0.2 mg to be considered acceptable.

- Blank determinations will be performed on each lot of acetone rinse solution. Blank residue must be ≤0.01 mg/g or 0.001 percent of the blank weight.

9.1.3 Quality Control Procedures for Velocity/Volumetric Flow Rate Determination

Data required to determine the volumetric gas flow rate will be collected using the methodology specified in EPA Method 2 (3). Quality control will focus on the following procedures:

- The S-type pitot tube will be visually inspected before and after sampling.
- Both the low pressure and high pressure legs of the pitot tube will be leak checked before and after sampling.
- The oil manometer gauge used to indicate the differential pressure (ΔP) across the S-type pitot tube will be leveled and zeroed.
- The number and location of the sampling traverse points will be checked before taking measurements.
- The temperature measurement system will be visually checked for damage and operability by measuring the ambient temperature prior to each traverse.
- All sampling data and calculations will be recorded on preformatted data sheets.

9.1.4 Sampling Quality Control Procedures for Moisture Determination

The moisture content of the gas streams will be determined using the technique specified in EPA Method 4 (4). The following internal QC checks will be performed as part of the moisture determinations:

- Each impinger will be weighted to the nearest 0.1 grams before and after sampling.
- The sampling train, including impingers, will be leak checked before and after each run.
- Ice will be maintained in the ice bath throughout the run.
- Any unusual conditions or occurrences will be noted during each run on the appropriate data form.

- The field sampling team leader will review sampling data sheets daily during testing.

9.1.5 Quality Control Procedures for Molecular Weight Determinations

Samples to be used for determination of stack gas molecular weight will be collected using the integrated sampling technique specified in EPA Method 3 (4). Quality control for the Method 3 sampling will focus on the following:

- The sampling train will be leak-checked before and after each sampling run.
- A constant sampling rate (±10 percent) will be used in withdrawing a sample.
- The sampling train will be purged prior to sample collection.
- The sampling port will be properly sealed to prevent air in leakage.

9.1.6 Quality Control Procedures for HCL Acid Train

The sample to be used for determining the HCL concentration in the flue gas will be obtained using a modified acid sampling train. Quality control will focus on the following:

- Prior to sampling, the HCL impinger train will be properly assembled for use. The first and second impingers will contain 0.1 NaOH solution. The third impinger will be dry while the last impinger will contain silica gel.
- The entire sampling train will be leak-checked before and after each run.
- The probe and sample line prior to the impinger train will be maintained above the dew point of the sample gas.
- Ice will be maintained in the ice bath throughout each run.
- Dry gas meter readings will be properly made at the start and end of sampling.
- A constant (i.e., within 10 percent) sampling rate will be maintained.

9.2 ANALYTICAL QUALITY CONTROL PROCEDURES

All analyses for this program will be performed using accepted laboratory procedures in accordance with the specified analytical protocols. Gas standards used for quantitation will be certified (±2 percent accuracy) standards or standards prepared according to EPA traceability Protocol #1 (8). Adherence to prescribed QC procedures will ensure data of consistent and measurable quality. Analytical quality control will focus upon the use of control standards to provide a measure of analytical precision. Also, specific acceptance criteria are defined for various analytical operations including calibrations, control standard analyses, drift checks, blanks, etc. Table 9-1 is a summary of QC requirements for the various analyses, including frequencies and acceptance criteria. The following general QC procedures will be incorporated into the analytical effort:

- The on-site testing team leaders will review all analytical data and QC data on a daily basis for completeness and acceptability.
- A master logbook will be maintained as described in Section 5.
- Analytical QC data will be tabulated using the appropriate charts and forms on a daily basis.
- Copies of the QC data tabulation will be submitted to the QA coordinator following each test, with all originals kept on file in the mobile laboratory.
- All hardcopy raw data (i.e., chromatograms, computer printouts, etc.) will be maintained in organized files in the mobile laboratory.

Specific analytical QC procedures for each of the instrumental analyses are discussed below.

9.2.1 Quality Control Procedures for Continuous Monitors

Continuous monitoring for CO, CO_2, O_2, SO_2, NO_x and THC will be performed using the various instruments discussed in Section 4.0. Quality control procedures for all of the instruments will be identical. The primary control check for the continuous monitors will be daily analysis of control standards. The control standards, which will be certified (±2 accuracy) standards, will be introduced upstream of the sample conditioning

TABLE 9-1. SUMMARY OF ANALYTICAL QUALITY CONTROL CHECKS, FREQUENCIES, ACCEPTANCE CRITERIA AND CORRECTIVE ACTION

Parameter/Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
CO/CO_2 Analysis (NDIR)	Linearity Check (zero plus two upscale)	Once per site (prior to testing)	Correlation coefficient ≥0.9950	(1) Repeat linearity check. (2) If still unacceptable, make adjustments as necessary. (3) Repeat linearity check.
	Single Point RF	Daily (prior to testing)	Agreement within 20% of previous multipoint RF	(1) Repeat single point RF check. (2) If still unacceptable, perform new multipoint calibration.
	Analytical Blank	Daily (prior to testing)	Zero value ≤1% of span	(1) Adjust instrument zero. (2) Repeat blank analysis. (3) If still unacceptable, use blank correction factor.
	Control Sample Analysis	Daily (prior to testing)	Agreement of daily value within 10% of running mean	(1) Repeat control sample analysis. (2) If still unacceptable, perform single point RF check.
	Drift Check, Single Point	Daily (at conclusion of testing)	RF agreement within 10% of RF for single point check	(1) Repeat drift check. (2) If still unacceptable, quanitate samples assuming linear drift over test day.
O_2 Analysis (Paramagnetic)	Linearity Check (zero plus two upscale points)	Once per site (prior testing)	Correlation coefficient ≥0.9950	(1) Repeat linearity check. (2) If still unacceptable, make necessary adjustments. (3) Repeat linearity check.
	Leak Check (Sampling System)	Once per site (prior to testing)	Zero O_2 value of ≤0.5% O_2	(1) Inspect sampling system and make adjustments as necessary. (2) Repeat leak check. (3) If still unacceptable, derive and apply acceptable correction factor.
	Single Point RF	Daily (prior to testing)	Agreement within 20% of previous multipoint RF	(1) Repeat single point RF check. (2) If still unacceptable, perform new multipoint calibration.
	Analytical Blank	Daily (prior to testing)	Zero value ≤1% of span	(1) Adjust instrument zero. (2) Repeat blank analysis. (3) If still unacceptable, use blank correction factor.
	Control Sample Analysis	Daily (prior to testing)	Agreement of daily value within 10% of running mean	(1) Repeat control sample analysis. (2) If still unacceptable, perform single point RF check.
	Drift Check, Single Point	Daily (at conclusion of testing)	RF agreement within 10% of RF for single point check	(1) Repeat drift check. (2) If still unacceptable, quanitate samples assuming linear drift over test day.

TABLE 9-1. (Continued)

Parameter/Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
NO_x Analysis (Chemiluminecence)	Linearity Check (zero plus two upscale points)	Once per site (prior testing)	Correlation coefficient ≥0.9950	(1) Repeat linearity check. (2) If still unacceptable, make adjustments as necessary. (3) Repeat linearity check.
	Single Point RF	Daily (prior to testing)	Agreement within 20% of previous multipoint RF	(1) Repeat single point RF check. (2) If still unacceptable, perform new multipoint calibration.
	Analytical Blank	Daily (prior to testing)	Zero value ≤1% of span	(1) Adjust instrument zero. (2) Repeat blank analysis. (3) If still unacceptable, use blank correction factor.
	Control Sample Analysis	Daily (prior to testing)	Agreement of daily value within 10% of running mean	(1) Repeat control sample analysis. (2) If still unacceptable, perform single point RF check.
	Drift Check, Single Point	Daily (at conclusion of testing)	RF agreement within 10% of RF for single point check	(1) Repeat drift check. (2) If still unacceptable, quanitate samples assuming linear drift over test day.
THC Analysis (FID)	Linearity Check (zero plus two upscale points)	Once per site (prior testing)	Correlation coefficient ≥0.9950	(1) Repeat linearity check. (2) If still unacceptable, make necessary adjustments. (3) Repeat linearity check.
	Single Point RF	Daily (prior to testing)	Agreement within 20% of previous multipoint RF	(1) Repeat single point RF check. (2) If still unacceptable, perform new multipoint calibration.
	Analytical Blank	Daily (prior to testing)	Zero value ≤1% of span or 1% span, whichever is smaller	(1) Adjust instrument zero. (2) Repeat blank analysis. (3) If still unacceptable, use blank correction factor.
	Control Sample Analysis	Daily (prior to testing)	Agreement of daily value within 10% of running mean	(1) Repeat control sample analysis. (2) If still unacceptable, perform single point RF check.
	Drift Check, Single Point	Daily (at conclusion of testing)	RF agreement within 10% of RF for single point check	(1) Repeat drift check. (2) If still unacceptable, quanitate samples assuming linear drift over test day.
	Sampling System Blank	Once per site (prior to testing)	Zero value of ≤5 ppmv or 1% of span, whichever is smaller	(1) Perform cleanup as necessary. (2) Repeat blank analysis. (3) If still unacceptable, use blank correction factor.

TABLE 9-1. (Continued)

Parameter/Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
SO_2 Analysis (Pulsed Flouresence)	Linearity Check (zero plus two upscale points)	Once per site (prior testing)	Correlation coefficient ≥0.9950	(1) Repeat linearity check. (2) If still unacceptable, make necessary adjustments. (3) Repeat linearity check.
	Single Point RF	Daily (prior to testing)	Agreement within 20% of previous multipoint RF	(1) Repeat single point RF check. (2) If still unacceptable, perform new multipoint calibration.
	Analytical Blank	Daily (prior to testing)	Zero value ≤1% of span	(1) Adjust instrument zero. (2) Repeat blank analysis. (3) If still unacceptable, use blank correction factor.
	Control Sample Analysis	Daily (prior to testing)	Agreement of daily value within 10% of running mean	(1) Repeat control sample analysis. (2) If still unacceptable, perform single point RF check.
	Drift Check, Single Point	Daily (at conclusion of testing)	RF agreement within 10% of RF for single point check	(1) Repeat drift check. (2) If still unacceptable, quanitate samples assuming linear drift over test day.
Polychlorinated Biphenyls (PCB) (GC/MS)	Linearity Check (Multipoint calibration)	Once prior to sample analysis	Correlation Coefficient ≥0.90	(1) Repeat linearity check. (2) If still unacceptable, make necessary adjustments. (3) Repeat linearity check.
	Single Point Check	Daily (prior to analysis)	Agreement within 15% of value predicted from multipoint calibration curve	(1) Repeat single point check. (2) If still unacceptable, perform new multipoint calibration.
	Control Sample Analysis	Daily (prior to analysis)	(See Table 9-3)	(1) Repeat control sample analysis. (2) If still unacceptable, make necessary adjustment, and repeat single point check.
	Duplicate Sample Analysis	20% of samples	Percent difference within 50%	(1) Repeat analysis.
Chlorobenzenes (GC/MS)	Same as PCB	Same as PCB	Same as PCB	(1) Same as PCB.
Chlorophenols (GC/MS)	Same as PCB	Same as PCB	Same as PCB	(1) Same as PCB.
HCl and Chlorides (Ion Chromatograph, Atomic Absorption)	Linearity Check (Multipoint calibration)	Twice (prior to and upon completion of analyses	Correlation coefficient ≤0.9950 and slope within 10% of running mean for previous six determinations	(1) Repeat linearity check. (2) Prepare new standards. (3) Service instrument.

TABLE 9-1. (Continued)

Parameter/Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
	Duplicate Sample Analysis	20% of samples	Agreement between duplicates of 5% of the mean	(1) Repeat analyses.
Fixed Gases (Shimadzu 3BT)	Duplicate Standard Analysis	Twice (prior to and upon completion of analyses	Agreement of analyses within 5% (CV)	(1) Repeat analyses. (2) If still unacceptable, service instrument. (3) Repeat analyses.
	Duplicate Control Sample Analysis	Once daily after calibration	Agreement of analyses within 5% (CV) and agreement of daily mean within 10% of running mean	(1) Repeat analyses. (2) If still unacceptable, repeat duplicate standard analysis.

system for all monitors except for the THC analyzer. The THC control standard will be introduced directly into the instrument. The control standards will be separate standards from those used for instrument calibration. The acceptance criteria for the daily control standard determination will be agreement within ±10 percent of the overall (running) mean for previous analyses. Results of the control sample analyses for CO, CO_2, O_2, NO_x, SO_2 and THC will be tabulated and plotted daily on a control chart. An example of the control chart which will be used is shown in Figure 9-1.

Prior to sampling at each site, a three-point (zero plus two upscale) calibration will be performed on each instrument to provide a linearity check. The acceptance criteria for the linearity check will be a correlation coefficient, r, ≥ 0.9950 for all continuous monitors.

An analytical blank will be performed daily prior to sampling. The acceptance criteria for the analytical blank for parameters other than THC will be a zero value ≤1 percent of the span. For the THC analysis, the blank acceptance criteria will be a zero value of ≤5 ppmv or ≤1 percent of span, whichever is smaller. Two single point calibrations will also be performed daily. The response factor (RF) for the first will be compared to the average multipoint RF for the calibration described above. The RF for the second, performed at the conclusion of the days testing, will be compared to the first RF, serving as a drift check. If the two single point RFs agree within 10 percent (CV) the drift check will be considered acceptable and the first RF will be used for sample quantitation. If agreement is not within 10 percent, the first RF and the second RF will be used for sample quantitation assuming a linear drift throughout the test day.

9.2.2 Quality Control Procedures for GC/MS Analysis

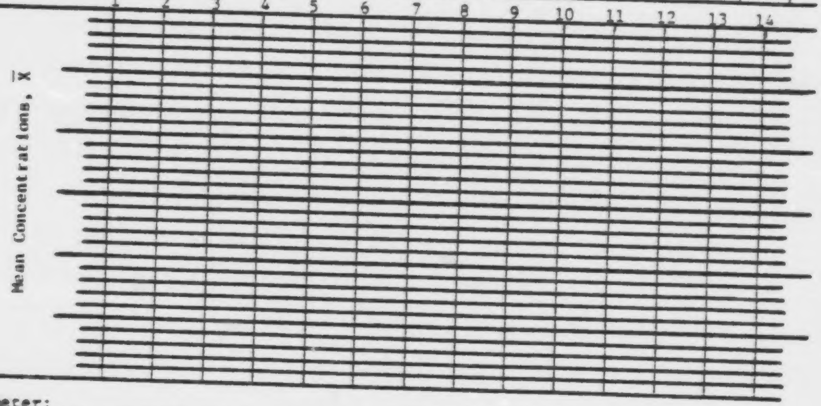
Internal quality control checks in the GC/MS analysis will consist of daily calibration checks and monitoring an internal standard on each calibration check and on each sample. A 5-point calibration curve and response factor for the compounds of interest will be developed. In order for the calibration to be valid, the regression coefficient must be greater than 0.90. A single calibration check will be made daily. The response of

QC STANDARD ANALYSIS RECORD

Contract ____________________
Site ____________________
Method/Instrument ____________________

Analyst ____________________
Analyte Units ____________________

Parameter:															
Date															
Input Conc.															
Measured Conc.	1														
	2														
	3														
Mean Conc.	$\bar{X}$														
CV															



Parameter:															
Date															
Input Conc.															
Measured Conc.	1														
	2														
	3														
Mean Conc.	$\bar{X}$														
CV															

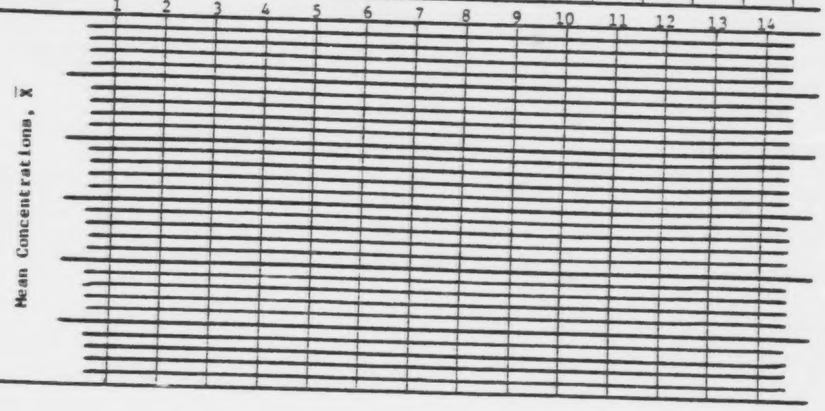


Figure 9-1. Example of Control Standard Analysis Record

the daily calibration check must fall within ±15% of the value predicted from the multipoint calibration curve, or a new set of calibration standards must be made up, and a new calibration curve derived.

9.2.2.1 Optimization of the GC/FID and GC/MS Procedures. GC operating conditions will be optimized by analyzing solutions containing a variety of the candidate compounds by the GC/FID technique. The column head pressure is adjusted appropriately to maximize the FID response to the test mixtures. These adjustments are used to select the optimum carrier gas velocity.

Having established GC operating conditions by the GC/FID procedure, the method is then applied to the determination of the candidate compound by GC/MS. The mass spectrometer is operated in a full-mass-scanning range (35 to 450 amu) in the EI mode. The scan time is maintained at 1 second to enable the collection of each scans to characterize each capillary GC peak.

The GC/FID and GC/MS procedure will include calibration utilizing standard solutions of the compounds. Five-point calibration curves are prepared for each compound determined by gas chromatography. Each response of the FID and/or MS response (relative to the quantitation standard) as a column will be plotted.

In addition to the use of standard solutions for the calibration, the performance of the GC/MS system will be checked with decafluorotriphenylphosphene (DETPP) on a daily basis as a quality control check according to the requirements given in EPA Method No. 625. Acceptance criteria for the tuning standard are shown in Table 9-2.

Capillary columns will be evaluated and characterized utilizing Grob type mixtures. The columns will be evaluated on installation and at least once per week thereafter. In addition, if column performance deteriorates, steps must be taken to improve the performance or the column must be replaced. The column parameters which will be monitored are resolution, peak asymmetry and column acidity/basicity. A change of 50% from the original values for one or more of these parameters will initiate remedial action.

Table 9-2. TUNE CRITERIA FOR DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Mass	Ion abundance criteria[a]
51	30% to 60%
68	<2% of mass 69
70	<2% of mass 69
127	40% to 60% of mass 198
197	<1% of mass 198
198	100% (base peak)
199	5% to 9% of mass 198
275	10% to 30% of mass 198
365	<1% of mass 198
441	Present, but less than mass 443
442	<40% of mass 198
443	17% to 23% of mass 442

[a] All values in percent abundance relative to mass 198, unless otherwise stated.

9.2.2.2 Surrogate Spiking. The number of samples required to establish the precision and accuracy of a method can be significantly reduced by utilizing surrogate compounds as performance indicators. By utilizing stable isotope-labeled compounds, method performance can be monitored on a routine basis without the cost of additional spiked analyses. Stable isotope-labeled compounds that have the same physical and chemical characteristics as the analyte, and that are not present in the samples are ideal choices for determining method performance. Table 9-3 gives a format for reporting the results of the surrogate spike.

The recoveries of the stable isotope-labeled surrogate compounds are used as the primary measurement of method analysis precision. In addition, the spiking of surrogate standards in all sample field blanks, method blanks and actual samples prior to extractions can be used to determine whether any sample matrix effects or other analytical problems affect the accuracy of the analyses.

9.2.2.3 Quality Control Samples. Data generated from daily control samples are to be used to update control charts and, by addition to the existing data base, to refine the detection limit of the analytical method as well as the estimates of precision and accuracy.

Quality control samples will be inserted at random in a sample analysis series. At least one control sample is to be included with each lot of samples. The types of control samples are chosen to minimize the number of control samples and maximize the quality control data obtained from the analytical system. For example, a spike of a previously analyzed combustion sample, or blank XAD extract containing no detectable analyte may exhibit matrix effects that will not be demonstrated by a spike in a standard solvent.

9.2.3 Quality Control Procedures for Ion Chromatograph and Atomic Absorption Analyses

The ion chromatograph (IC) will be used to determine Cl^- concentrations in the impinger catch from the HCL acid train and selected process samples. Some acid train samples will also require determination of sulfate (SO_4^{--}) ion concentrations by IC and sodium ion concentrations by atomic absorption

Table 9-3. SURROGATE RECOVERIES

Surrogate(s)	Target* concentration (ug)	Average found value	deviation	precision	accuracy
Naphthalene-d_8					
3-Bromobiphenyl					
2,2',5,5'-Tetrabromobiphenyl					
2,2',4,4',6,6'-Hexabromobiphenyl					
Phenol-d_5					
2-Chlorophenol-d_4					
Dichlorobenzene-d_4					

*To be determined based on sample matrix.

$$\text{Percent relative standard deviation} = \frac{S}{\bar{X}} \times 100$$

where:

S = Standard deviation
$\bar{X}$ = Average concentration.

$$\text{Percent recovery} = \frac{\bar{X}}{TC} \times 100$$

where:

$\bar{X}$ = Average found concentration at the TC.
TC = Target concentration

spectroscopy. These analysis methods involve the generation of a standard calibration curve. This curve is a linear plot of analyte concentration versus instrument response (conductivity or absorbance). The calibration curve is generated using response data from analysis of the blanks and calibration standards. This data is plotted mathematically using linear regression to get the slope, Y-intercept, and correlation coefficient of the calibration curve. The validity of the resulting curve may be assessed by examining these three items. The slope of the curve is related to response sensitivity. Any marked deviation from the average slope for the method and/or parameter of interest indicates that a change in sensitivity has occurred. The acceptance criterion for slope will be agreement with running mean slope for six most recent determinations within 10 percent. The Y-intercept of the curve should ideally be equal to zero, i.e., instrument response to a blank should be zero and the calibration curve should pass through the origin. In practice, the curve rarely passes exactly through the origin.

The correlation coefficient is indicative of the linearity of the curve. According to Beer's law, the response should be directly proportional to concentration. Perfect correlation of the X and Y data points is indicated by a correlation coefficient of 1.0. An acceptable calibration curve will have a correlation coefficient ≥ 0.9950.

- Calibration curves will be generated according to the frequencies indicated in Table 9-1, and evaluated for acceptability as discussed above.
- The QC standards will be analyzed according to the frequency indicated in Table 9-1.
- Blanks will be analyzed for each parameter and will be incorporated into the calibration curves as the X and Y zero points.
- Duplicate samples will be analyzed as indicated in Table 9-1.
- The results of QC standard analyses will be plotted on control charts (Figure 9-1), on a daily basis.

- Results for duplicate analyses will be tabulated using the form shown in Figure 9-2.
- The acceptability criteria for the calibration curve and QC standard analyses indicated in Table 9-1 must be met before sample analysis may proceed.
- The slope and correlation coefficient of each calibration curve will be tabulated on a daily basis and compared to results from previous days.
- All samples not analyzed immediately will be properly preserved and stored.

9.2.4 Quality Control for Fixed Gas Analysis

Fixed gas analysis for molecular weight determination will be based Modified Method 3 (Shimadzu 38T analyzer). Quality control procedures will includes one or more single point calibrations immediately prior to and upon completion of sample analysis. The acceptance criteria for the single point calibrations will be duplicate analysis within ≤5 percent (CV). A control standard will also be analyzed in duplicate on a daily basis to provide an estimate of precision and day-to-day variability. The acceptance criteria for the control standard will be ≤5 percent (CV) and agreement of daily mean within 10 percent of running mean.

9.3 QUALITY CONTROL PROCEDURES FOR PROCESS SAMPLE COLLECTION

Various types of process samples will be collected for dioxin and precursor analysis during the Tier 4 study. Types of samples that may be required include the following, depending on the specific combustion source and emission control device:

- liquid fuels,
- solid fuels,
- sludges,
- ash slurry,
- makeup water,
- scrubber blowdown,
- process/cooling water,

CONTRACT ____________________
SITE ____________________
METHOD/INSTRUMENT ____________________

ANALYST ____________________
ANALYTE UNITS ____________________

Sample I.D.	Date	Analyte	Analyte	Analyte	Analyte	Analyte	Analyte	Analyte	Analyte	Pooled CVs
	CV									
	CV									
	CV									
	CV									
	CV									
	CV									
	CV									
	Pooled CVs									

Comments ____________________
____
____
____

Figure 9-2. Replicate analysis log.

- bottom ash,
- fly ash, and
- soil from the plant site.

The following general QC procedures will apply to the collection of these samples:

- Sample locations will be selected to provide the most representative sample obtainable.
- The sample technique used will be appropriate for the particular sample location.
- Where possible, samples of streams with widely varying composition and flow will be composited on a weighted basis.
- All samples will be collected using a technique appropriate for the particular sample type.
- Sampling containers and equipment will be properly cleaned prior to use in the field.
- A single set of sample bottles will be used for each sampling point to avoid cross-stream contamination of samples.
- Slurry and liquid samples will be collected only after the sample line and valve are thoroughly flushed.
- Samples will be logged into the master logbook immediately after collection.
- The field team leader will review the master logbook on a routine basis to ensure that all required samples have been collected.
- Samples will be transferred to appropriate storage containers immediately after collection.

SECTION 10

PERFORMANCE AND SYSTEMS AUDITS

An audit is an independent assessment of data quality. This independent assessment is achieved by using apparatus and/or standards that are different from those used by the regular field crew. Routine quality assurance checks by an independent field team are necessary for ensuring that data quality will meet the specified objectives.

During the field testing portion of this project, the QA coordinator will be on site for two or three days to perform independent performance and systems audits. If possible, the QA audits will be conducted during testing at the second site. The function of the field auditor will be to:

- observe procedures and techniques of the field sampling crew,
- check and verify records of calibration,
- assess the effectiveness of and adherence to the prescribed QC procedures,
- review document control procedures,
- identify and correct any weaknesses in the sampling/analytical approach and techniques, and
- assess the overall data quality of the various sampling/analytical systems.

The auditor will observe and document the overall performance of the personnel responsible for each of the various on-site sampling and analytical efforts (systems audits). Audit standards, such as standard gas mixtures containing representative flue gas components and test equipment which are traceable to acceptable reference standards will be used to assess the performance of each analytical method and/or measurement device (performance audit). Dioxin precursor audit samples will be submitted to the Radian RTP laboratory with samples collected from the test site. The performance audit of Methods 1 and 2 will include an independent determination of velocity by the auditor using differential pressure and temperature measurement devices different from those used by the field testing team. The modified Method 5, Method 5 and Method 4 audits will include a check of the dry gas meter calibration using a standard dry gas meter which is traceable to a primary displacement standard. Performance audit activities are summarized in Table 10-1.

The systems audits will consist of observations and documentation of all aspects of the on-site sampling and analytical activities. Checklists which delineate the critical aspects of each methodology will be used by the Radian auditor during the audit and will serve to document all observations. An example systems audit checklist is illustrated in Figure 10-1. In addition to evaluating sampling and analytical procedures and techniques, the systems audit will emphasize review of all recordkeeping and data handling systems including:

- calibration documentation for both instruments and apparatus;
- completeness of field data forms;
- field data review and validation procedures;
- field data storage and filing procedures;
- sample logging procedures;
- field laboratory custody procedures;
- documentation of quality control data (control charts);
- documentation of field maintenance activities; and
- review of malfunction reporting procedures.

Upon completion of the audit, the auditor will discuss any specific weaknesses with the field team leader and make recommendations for corrective action. An audit report will subsequently be prepared and distributed to the task leaders and the Project Director. This report will outline the audit approach and present a summary of results and recommendations.

TABLE 10-1. SUMMARY OF PERFORMANCE AUDIT ACTIVITIES

Parameter	Method	Example Data Set	Audit Gas Analysis	Equipment Calibration Check
Flue Gas Dioxins	Modified Method 5			*
Particulate	Method 5			*
HCL	HCL Acid Train			*
Velocity/Volumetric Flowrate	Methods 1 & 2	*		
Moisture	Method 4	*		*
Molecular Weight (Fixed Gas Analysis)	Method 3	*	*	
Ambient XAD	Resin Adsorption			*
CO/CO_2	NDIR		*	
O_2	Paramagnetic		*	
NO_x	Chemiluminescence		*	
SO_2	Pulsed Flourescence		*	
THC	FID		*	

MODIFIED METHOD 5 SYSTEMS AUDIT CHECKLIST

Site: ______________________ Date: ______________________

Contract: ______________________ Auditor: ______________________

Yes	No	Comments	Operation
			PRESAMPLING PREPARATION
____	____	______________________	1. Knowledge of process conditions.
____	____	______________________	2. Calibration of pertinent equipment prior to each field test (especially nozzles, dry gas meter, temperature sensors).
____	____	______________________	3. Appropriate number and location of sample traverse points.
____	____	______________________	4. Filter properly handled during pretreatment and loading.
____	____	______________________	5. XAD traps properly handled during pretreatment and loading.
____	____	______________________	6. Appropriate size nozzle selected per isokinetic sampling and gas velocity considerations.
____	____	______________________	7. Adequate identification procedures used for filters.
____	____	______________________	8. Adequate identification procedures for XAD traps.
____	____	______________________	9. Date of precleaning for XAD resin.
____	____	______________________	10. Date of precleaning for filter elements.
____	____	______________________	11. Sampling train properly assembled.
____	____	______________________	12. Adequate facilities, spare parts, and support equipment available.

Figure 10-1. Modified Method Five Audit Checklist

Modified Method 5 Systems Audit Checklist (Continued)

Yes	No	Comments	Operation
			SAMPLING OPERATIONS
			1. Initial leak check performed.
			2. Probe maintained at proper temperature (248°F).
			3. Filter holder maintained at proper temperature (248 ± 25°F).
			4. Appropriate data recorded during sampling run.
			5. Proper flow rate maintained for isokinetic sampling at each point (within ±10%).
			6. Probe placed into and removed from stack with care taken to avoid scraping port and/or duct walls.
			7. Sample train leak checked at conclusion of run.
			POSTSAMPLING OPERATIONS
			1. Sufficient sample volume collected.
			2. Nozzle rinse performed properly (acetone, hexane x 3).
			3. Proper handling procedure observed in unloading filter holder.
			4. Field blanks for filter and XAD submitted for analysis.
			5. Chain-of-custody documentation completed for each component of train.
			6. Data and pertinent observations properly recorded.

Figure 10-1. Modified Method Five Audit Checklist (Continued)

Modified Method 5 Systems Audit Checklist (Continued)

Yes	No	Comments	Operation
			POSTSAMPLING OPERATIONS (Continued)
			7. Adequate data reduction procedures.
			8. Blank train constructed, allowed to sit for at least 3 hours, disassembled and submitted for analysis.

COMMENTS:

Figure 10-1. Modified Method Five Audit Checklist (Continued)

SECTION 11

PREVENTIVE MAINTENANCE

Prior to this field program, all sampling and analytical systems will be assembled and checked for proper operation. At this time, any worn or inoperative components will be identified and replaced.

In addition to the equipment required to provide the field measurements, certain spares will be taken to the field to minimize down time if equipment failure should occur. These spares include: pump, dry gas meter, rotameter, glassware, impingers, heating elements, pipe fittings, Tedlar® bags, stainless steel tubing, Teflon® tubing, differential pressure gauges, pressure gauges, GC columns and packing materials, stainless steel canisters and miscellaneous hardware.

SECTION 12

ASSESSMENT OF PRECISION, ACCURACY AND COMPLETENESS

The performance audits and QC analyses conducted during the Tier 4 test program are designed to provide a quantitative assessment of the measurement system data. The two aspects of data quality which are of primary concern are precision and accuracy. Accuracy reflects the degree to which the measured value represents the actual or "true" value for a given parameter, and includes elements of both bias and precision. Precision is a measure of the variability associated with the measurement system. The completeness of the data will be evaluated based upon the valid data percentage of the total tests conducted.

Precision of the measurement data for the continuous monitoring analyses and for the Method 3 fixed gas analyses will be based upon replicate analyses (replicability) and control sample analyses (repeatability). Variability will be expressed in terms of the coefficient of variation (CV) for the repeat analyses where,

$$CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\%$$

This term is independent of the error (accuracy) of the analyses and reflects only the degree to which the measurements agree with one another, not the degree to which they agree with the "true" value for the parameter measured. The CV is in units of percent since it is the standard deviation of the mean expressed as percent of the mean (relative standard deviation).

For analysis other than the GC/MS, analytical accuracy will be quantitated based upon the performance audit results. The audit data will be summarized in terms of "relative error," or "%Δ." This reflects the degree to which the measured value agrees with the actual value, in terms of percent of the actual value:

$$\text{Relative Error } (\%\Delta) = \frac{\text{Measured Value} - \text{Actual Value}}{\text{Actual Value}} \times 100$$

This way of expressing accuracy allows for the comparison of accuracy at different levels (e.g., different concentrations), and for different parameters of the same type (e.g., different compounds analyzed by the same method).

For the GC/MS precursor analyses, accuracy will be quantitated based on the quantity of surrogate standards spiked onto the samples prior to extraction/analysis. The relative error or percent Δ will be calculated from the spiked value:

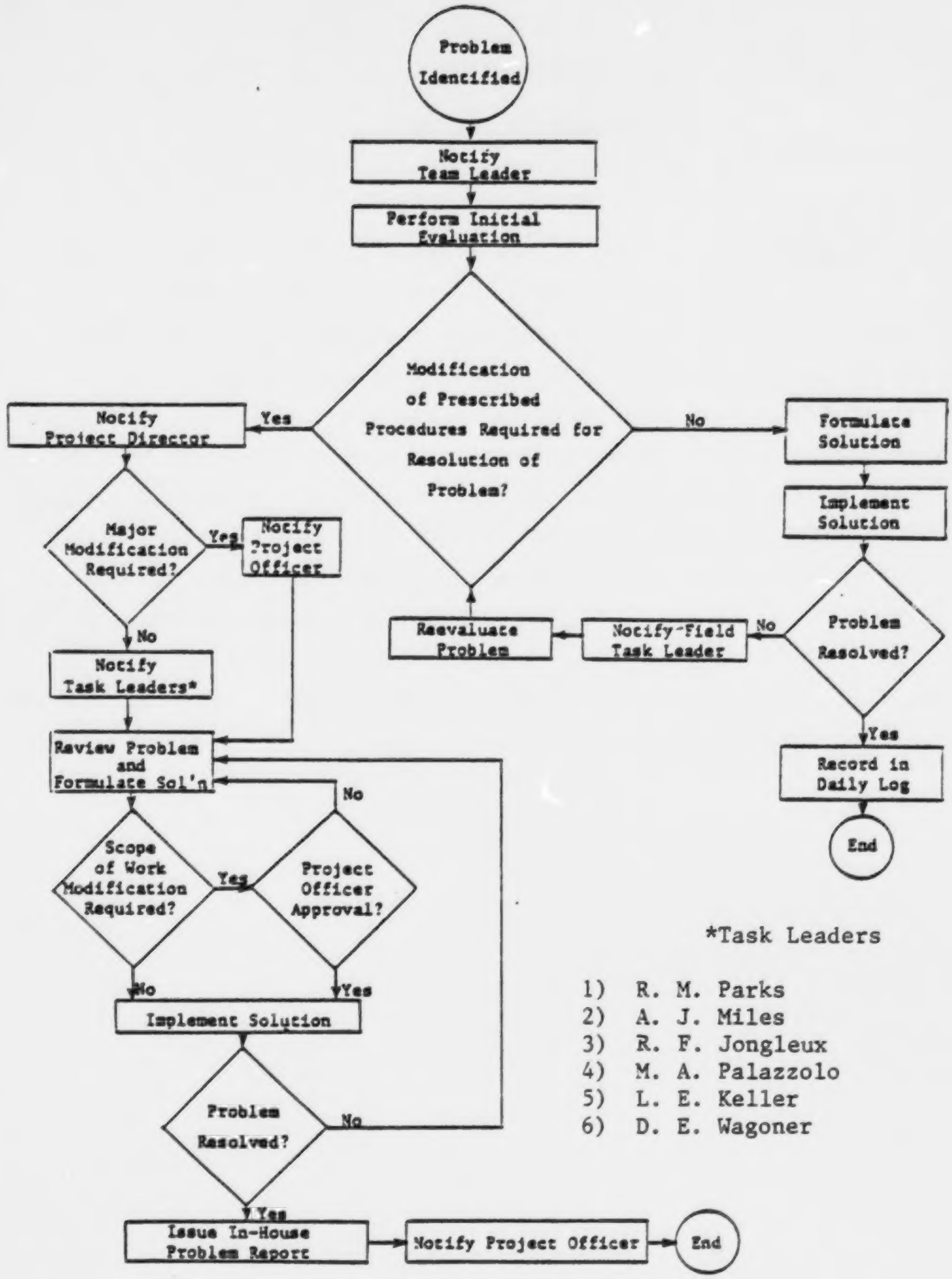
$$\text{Relative Error } (\%\Delta) = \frac{\text{Measured Value} - \text{Spiked Value}}{\text{Spiked Value}} \times 100$$

Precision and accuracy of the velocity/volumetric flow rate and moisture determinations will not be directly measured. The systems audits will be used to define the acceptability of the measurement data. If the data are judged to be acceptable based on compliance with specified test procedures, precision values of 6.0 percent and 10 percent for volumetric flow rate and moisture, respectively, will be assumed. Accuracy will be assumed to be ±10 percent for both measurements using the same acceptability criteria.

SECTION 13

CORRECTIVE ACTION

During the course of the Tier 4 test program it will be the responsibility of the field testing team leaders to see that all measurement procedures are followed as specified and that measurement data meet the prescribed acceptance criteria. In the event a problem arises, it is imperative that prompt action be taken to correct the problem(s). The field testing team leaders will initiate corrective action in the event that QC results exceed acceptability limits. Corrective action may also be initiated by the team leaders upon identification of some other problem or potential problem. Corrective action may be initiated by the QA coordinator based upon QC data or audit results. The corrective action scheme is shown in the form of a flow chart in Figure 13-1. Acceptability limits and prescribed corrective action related to the various internal QC checks are discussed in Section 9 and are summarized in Table 9-1.


Problem Identified
Notify Team Leader
Perform Initial Evaluation
Modification of Prescribed Procedures Required for Resolution of Problem?
Yes
No
Notify Project Director
Major Modification Required?
Yes
Notify Project Officer
No
Notify Task Leaders*
Review Problem and Formulate Sol'n
No
Scope of Work Modification Required?
Yes
Project Officer Approval?
No
Yes
Implement Solution
Problem Resolved?
No
Yes
Issue In-House Problem Report
Notify Project Officer
End
Formulate Solution
Implement Solution
Problem Resolved?
No
Notify Field Task Leader
Reevaluate Problem
Yes
Record in Daily Log
End

*Task Leaders

1) R. M. Parks
2) A. J. Miles
3) R. F. Jongleux
4) M. A. Palazzolo
5) L. E. Keller
6) D. E. Wagoner

Figure 13-1. Corrective Action Flow Scheme

SECTION 14

QUALITY ASSURANCE REPORTING

Effective management of a field sampling and analytical effort requires timely assessment and review of field activities. This will require effective interaction and feedback between the field team leaders, the Project Director and the QA coordinator.

Data summaries will be prepared immediately following the completion of each test. Copies of the QC data summary forms shown in Section 9 will be sent to the QA coordinator, Mr. D. L. Lewis, after each test. The field testing team leaders will be responsible for submitting the QC data summaries in a timely manner. In addition to these weekly data summaries, the field team leaders will provide the QA coordinator and the Project Director with letter format status reports immediately following each test which address the following:

- summary of activities and general program status,
- summary of calibration data,
- summary of unscheduled maintenance activities,
- summary of corrective action activities,
- status of any unresolved problems,
- assessment and summary of data completeness, and
- summary of any significant QA/QC problems and recommended and/or implemented solutions not included above.

The information included in these periodic field reports will be incorporated into the site-specific test reports and final report.

The QA coordinator will prepare audit reports following each performance and systems audit which will address data accuracy, and the qualitative assessment of overall system performance. These reports will be submitted to the Program Manager, Project Director, and field team leaders. The project final report will include a separate QA/QC section which summarizes the audit results, as well as the QC data collected throughout the duration of the program.

Problems requiring swift resolution will be brought to the immediate attention of the Project Director via the malfunction reporting/corrective action scheme discussed in Section 13.

REFERENCES

1. EPA Reference Method 5, "Determination of Particulate Emissions from Stationary Sources," Appendix A to 40 CFR, Environmental Reporter, Bureau of National Affairs, Washington, DC, December 5, 1980. pp 41-47.

2. EPA Reference Method 2, "Determination of Stack Gas and Velocity and Volumetric Flow Rate (Type S Pitot Tube)," Appendix A to 40 CFR, Environmental Reporter, Bureau of National Affairs, Washington, D.C., December 5, 1980. pp. 25-33.

3. EPA Reference Method 4, "Determination of Moisture Content in Stack Gases," Appendix A to 40 CFR, Environmental Reporter, Bureau of National Affairs, Washington, D.C., December 5, 1980. pp. 36-41.

4. EPA Reference Method 3, "Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight," Appendix A to 40 CFR, Environmental Reporter, Bureau of National Affairs, Washington, D.C., December 5, 1980. pp. 33-36.

5. Radian Corporation. National Dioxin Study Tier 4 - Combustion Sources: Sample Procedures. (Draft Report, Prepared for U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA Contract No. 68-02-3513, Task 51). August 1984.

6. Versar, Inc. Sampling Guidance Manual for the National Dioxin Study. (Draft Final Report, Prepared for U. S. Environmental Protection Agency, Washington, DC. EPA Contract No. 68-01-6160, Work Assignment 8.7), July 1984.

7. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods. EPA-600-4-77-027b, Environmental Protection Agency, Research Triangle Park, N.C., August 1977.

8. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C., June 1978. 10 pages.

APPENDIX A

ASME MODIFIED METHOD FIVE PROCEDURES

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SAMPLING FOR THE DETERMINATION OF CHLORINATED ORGANIC COMPOUNDS IN STACK EMISSIONS

1. PRINCIPLE AND APPLICABILITY

1.1 Principle: Stack gases that may contain chlorinated organic compounds are withdrawn from the stack using a sampling train. The analyte is collected in the sampling train. The compounds of interest are determined by solvent extraction followed by gas chromatography/mass spectroscopy (GC/MS).

1.2 Applicability: This method is applicable for the determination of chlorinated organic compounds in stack emissions. The sampling train is so designed that only the total amount of each chlorinated organic compound in the stack emissions may be determined. To date, no studies have been performed to demonstrate that the particulate and/or gaseous chlorinated organic compounds collected in separate parts of the sampling train accurately describes the actual partition of each in the stack emissions. If separate parts of the sampling train are analyzed separately, the data should be included and so noted as in Section 2 below. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of intricacies of the operation of the prescribed sampling train and constraints of the analytical techniques for chlorinated organic compounds, especially PCDDs and PCDFs.

Note: This method assumes that the XAD-2 resin collects all of the compounds of interest from the stack emissions. Since the method at the present time has not been validated in the presence of all the other components present (HCl, high organic load) in the stack emission, it is recommended that appropriate quality control (QC) steps be employed until such validation has been completed. These QC steps may include the use of a backup resin trap or the addition of a representative labeled standard (distinguishable from the internal standard used for quantitation) to the filter and/or the XAD-2 in the field prior to the start of sampling. These steps will provide information on possible breakthrough of the compounds of interest.

2. REPORTABILITY

Recognizing that modification of the method may be required for specific applications, the final report of a test where changes are made shall include: (1) the exact modification; (2) the rationale for the modification; and (3) an estimate of the effect the modification will produce on the data.

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3. RANGE OF MINIMUM DETECTABLE STACK GAS CONCENTRATION

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of stack gas sampled and the detection limit of the analytical finish. The user shall determine for their system the minimum detectable stack gas concentration for the chlorinated organic compounds of interest. The minimum detectable stack gas concentration should generally be in the ng/m^3 or lower range.

4. INTERFERENCES

Organic compounds other than the compounds of interest may interfere with the analysis. Appropriate sample clean-up steps shall be performed. Through all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than polytetrafluorethylene (TFE®). Adhesives should not be used to hold TFE® liners on lids (but, if necessary, appropriate blanks must be run), and lubricating and sealing greases must not be used on the sampling train.

5. PRECISION AND ACCURACY

Precision and accuracy measurements have not yet been made on PCDD and PCDF using this method. These measurements are needed. However, recovery efficiencies for source samples spiked with compounds have ranged from 70 to 120%.[1,3]

6. SAMPLING RUNS, TIME, AND VOLUME

6.1 Sampling Runs: The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

6.2 Sampling Time: The sampling time must be of sufficient length to provide coverage of the average operating conditions of the source. However, this shall not be less than three hours (3).

6.3 Sample Volume: The sampling volume must be sufficient to provide the required amount of analyte to meet both the MDL of the analytical finish and the allowable stack emissions. It may be calculated using the following formula:

$$\text{Sample Volume} = A \times \frac{100}{B} \times \frac{100}{C} \times \frac{1}{D}$$

A = The analytical MDL in ng
B = Percent (%) of the sample required per analytical finish run
C = The sample recovery (%)

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D = The allowable stack emissions (ng/m^3)

Example: A = 0.050 ng; B = 10%; C = 50%; and D = 1 ng/m^3

$$SV = 0.05 \times \frac{100}{10} \times \frac{100}{50} \times \frac{1}{1} = 1 m^3$$

7. APPARATUS

Sampling Train: The train consists of nozzle, probe, heated particulate filter, and sorbent module followed by four impingers (Fig. 1). Provision is made for the addition of (1) a cyclone in the heated filter box when testing sources emitting high concentrations of particulate matter, (2) a large water trap between the heated filter and the sorbent module for stack gases with high moisture content, and (3) additional impingers following the sorbent module. If one of the options is utilized, the option used shall be detailed in the report. The train may be constructed by adaption of an EPA Method 5 train. Descriptions of the sampling train components are contained in the following sections.

7.1.1 Nozzle

The nozzle shall be made to the specifications of EPA Method 5. The nozzle may be made of nickel plated stainless steel, quartz, or borosilicate glass.

7.1.2 Probe

The probe shall be lined or made of TFE®, borosilicate, or quartz glass. The liner or probe extends past the retaining nut into the stack. A temperature controlled jacket provides protection of the liner or probe. The liner or probe shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum-tight connection without sealing greases.

7.1.3 Sample Transfer Lines (optional)

The sample transfer lines, if needed, shall be heat traced, heavy walled TFE® (1.3 cm [1/2 in.] O.D. x 0.3 cm [1/8 in.] wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line should be as short as possible and must be maintained at 120°C.

7.1.4 Filter Holder

Borosilicate glass, with a glass frit filter support and a glass-to-glass seal or TFE® gasket. A rubber gasket shall not be used. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

leave out
See new

~~[illegible]~~

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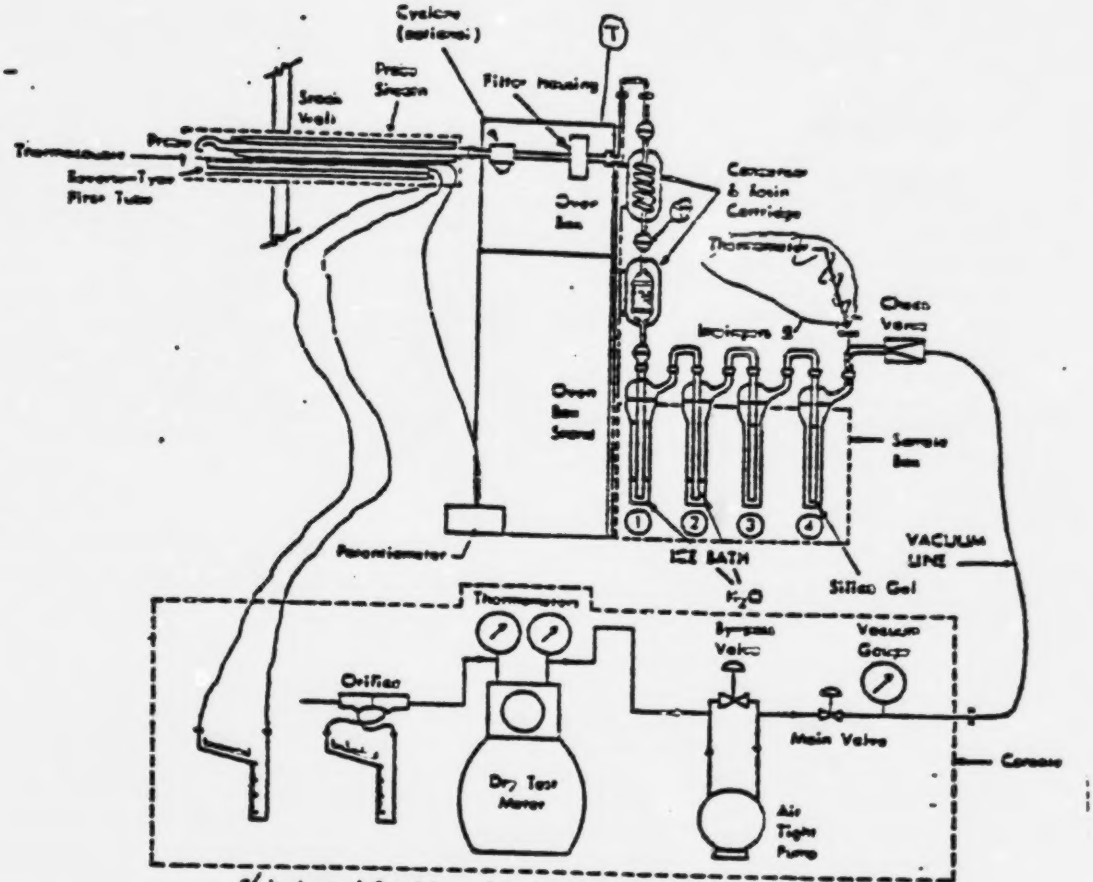
Cyclone (optional)
T
Probe Sheath
Stack Wall
Filter Housing
Probe
Thermocouple
Reverse-Type Pitot Tube
Oven Box
Condenser & Resin Cartridge
Thermometer
Oven Vent
Impingers a/
Oven Box Stand
Sample Box
1
2
3
4
Potentiometer
ICE BATH
H_2O
Silica Gel
VACUUM LINE
Thermometers
Bypass Valve
Vacuum Gauge
Orifice
Main Valve
Console
Dry Test Meter
Air Tight Pump

a/ Impingers ~~1, 2, and 4~~ are of the Modified Greenburg-Smith Type
~~Impinger 3 is of the Greenburg-Smith Design~~
Impinger 1 and 2 Contain 100 ml Water
Impinger 3 Empty
Impinger 4 Contains 200-300 Gram Silica Gel.
Impinger 1 is the hexane-rinsed back-up to the resin cartridge

add

Fig. 1 Modified EPA Method 5 Train for Organics Sampling
Source: Methods Manual Sampling and Analysis Procedures for Assessing Organics Emissions from Stationery Combustion Sources in Exposure Evaluation Division Studies, U.S. Environmental Protection Agency Report No. EPA-560-82-014 (January 1982).

7.1.5 Cyclone in Filter Box (optional)

The cyclone shall be constructed of borosilicate glass with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases.

7.1.6 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder (and cyclone, if used) during sampling of $120 \pm 14^{\circ}C$ ($248 \pm 25^{\circ}F$). A temperature gauge capable of measuring temperature to within $3^{\circ}C$ ($5.4^{\circ}F$) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

7.1.7 Solid Sorbent Module

Amberlite XAD-2® resin (XAD-2), confined in a trap, shall be used as the sorbent. The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum-tight seals without use of sealant greases (Figs. 2 and 3). The XAD-2 trap must be in a vertical position. It is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must be maintained at $\leq 20^{\circ}C$ ($68^{\circ}F$). Gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

7.1.8 Impingers

Four or more impingers with connecting fittings able to form leak-free, vacuum-tight seals without sealant greases when connected together, shall be used. All impingers are of the Greenburg-Smith design modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

7.1.9 Metering System

The metering system shall consist of a vacuum gauge, a leak-free pump, thermometers capable of measuring temperature to within $3^{\circ}C$ ($\sim 5^{\circ}F$), a dry gas meter with 2 percent accuracy at the required sampling rate, and related equipment, or equivalent.

7.1.10 Barometer

Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 Hg (0.1 in. Hg) shall be used.

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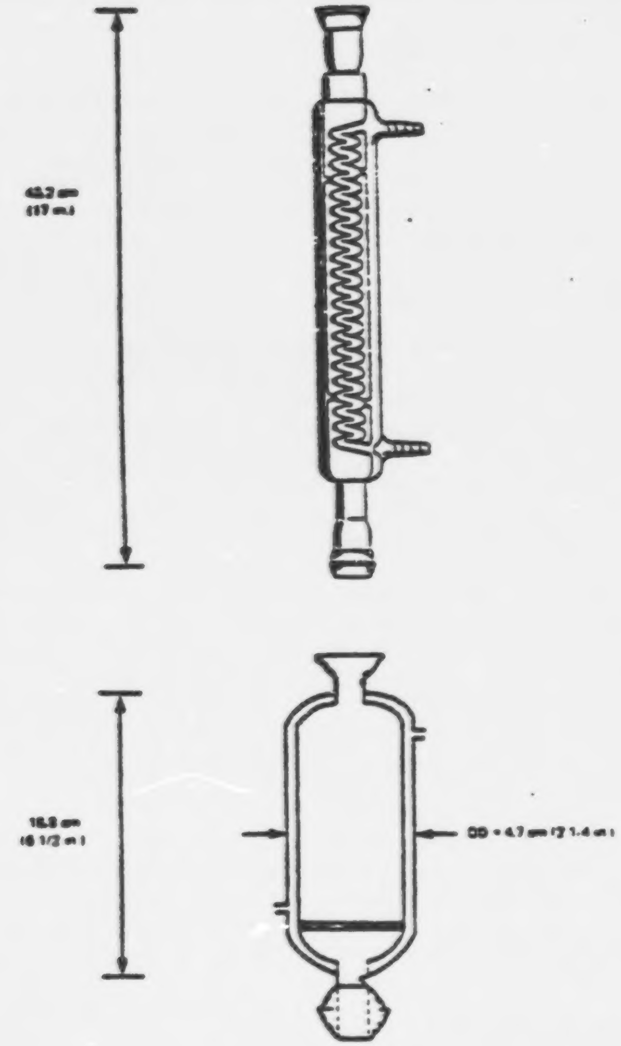
43.2 cm
(17 in.)
16.5 cm
(6 1/2 in.)
OD = 4.7 cm (1 7/8 in.)

Figure 2. Acceptable sorbent module design #1

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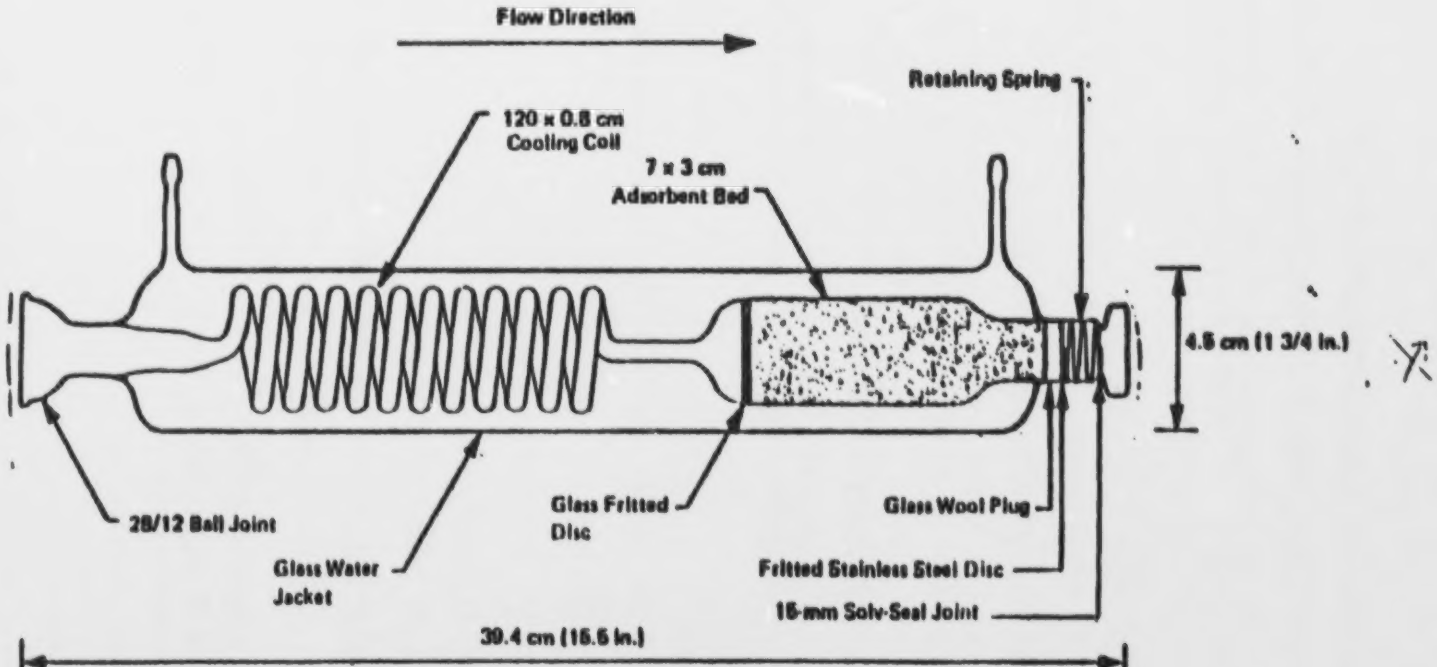
Flow Direction
Retaining Spring
120 x 0.8 cm Cooling Coil
7 x 3 cm Adsorbent Bed
4.5 cm (1 3/4 in.)
28/12 Ball Joint
Glass Water Jacket
Glass Fritted Disc
Glass Wool Plug
Fritted Stainless Steel Disc
15-mm Solv-Seal Joint
39.4 cm (15.5 in.)

Figure 3 Acceptable sorbent module design #2

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7.2 Sample Recovery, Supplies, and Equipment

7.2.1 Ground Glass Caps or Hexane Rinsed Aluminum Foil

To cap off adsorbent tube and the other sample-exposed portions of the train. If TFE® screw connections are used, then TFE® screw caps shall be used.

7.2.2 Teflon FEP® Wash Bottle

Three 500 ml, Nalgene No. 0023A59, or equivalent.

7.2.3 Probe and Transfer Line Brush

Inert bristle brush with stainless steel rod-handle of sufficient length that is compatible with the liner or probe and transfer line.

7.2.4 Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with TFE®-lined screw caps or wrapped in hexane rinsed aluminum foil.

7.2.5 Balance

Triple beam, Ohaus model 7505, or equivalent.

7.2.6 Aluminum Foil

Heavy duty, hexane-rinsed.

7.2.7 Precleaned Metal Can

To recover used silica gel.

7.2.8 Precleaned Graduated Cylinder, e.g., 250 ml

250 ml, with 2 ml graduations, borosilicate glass.

7.2.9 Liquid Sample Storage Containers

Precleaned amber glass bottles or clear glass bottles wrapped in opaque material, 1 L, with TFE®-lined screw caps.

8. REAGENTS

8.1 Sampling

8.1.1 Filter -- Fiberglass Reeve-Angel 934 AH or Equivalent

Prior to use in the field, each lot of filters shall be subjected to precleaning and a quality control (QC) contamination check to confirm that there are no contaminants present that will

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interfere with the analysis of analyte at the target detection limits.

If performed, filter precleaning shall consist of Soxhlet extraction, in batches not to exceed 50 filters, with the solvent(s) to be applied to the field samples. As a QC check, the extracting solvent(s) shall be subjected to the same concentration, cleanup and analysis procedures to be used for the field samples. The background or blank value observed shall be converted to a per filter basis and shall be corrected for any differences in concentration factor between the QC check (CF_{QC}) and the actual sample analysis procedure (CF_s).

$$\text{Blank value per filter} = \frac{\text{Apparent } \mu\text{g of analyte}}{\text{No. filters extracted}} \times \frac{CF_s}{CF_{QC}}$$

where:

$$CF = \frac{\text{Initial volume of extracting solvent}}{\text{Final Volume of concentrated extract}}$$

The quantitative criterion for acceptable filter quality will depend on the detection limit criteria established for the field sampling and analysis program. Filters that give a background or blank signal per filter greater than or equal to the target detection limit for the analyte(s) of concern shall be rejected for field use. Note that acceptance criteria for filter cleanliness depends not only on the inherent detection limit of the analysis method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

If the filters do not pass the QC check, they shall be re-extracted and the solvent extracts re-analyzed until an acceptably low background level is achieved.

8.1.2 Amberlite XAD-2 Resin

The cleanup procedure may be carried out in a giant Soxhlet extractor, which will contain enough Amberlite XAD-2® resin (XAD-2) for several sampling traps. An all glass thimble 55-90 mm OD x 150 mm deep (top to frit) containing an extra coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The XAD-2 must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse with 1 L H_2O for 1 cycle, then discard H_2O

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Water	Extract with H_2O for 8 hr
Methyl alcohol	Extract for 22 hr
Methylene chloride	Extract for 22 hr
Hexane	Extract for 22 hr

The XAD-2 must be dried by one of the following techniques.

(a) After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

A simple column with suitable retainers as shown in Fig. 4 will serve as a satisfactory column. A 10.2 cm (4 in.) diameter Pyrex pipe 0.6 m (2 ft. long) will hold all of the XAD-2 from the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum XAD-2 load at the exit of the column.

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95 cm (3/8 in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight consuming a full 160 L cylinder of liquid nitrogen.

As a second choice, high purity tank nitrogen may be used to dry the XAD-2. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidation may cause th

particles to break up.

(b) As an alternate, if the nitrogen process is not available, t

XAD-2 may be dried in a vacuum oven, if the temperature never exceeds 20°C.

The XAD-2, even if purchased clean, must be checked for both methylene chloride and hexane residues, plus normal blanks befor use.

(c) Storage of Clean XAD-2: XAD-2 cleaned and dried as prescri

above is suitable for immediate use in the field, provided it passes the QC contamination check described in (d), below. How ever, precleaned dry XAD-2 may develop unacceptable levels of

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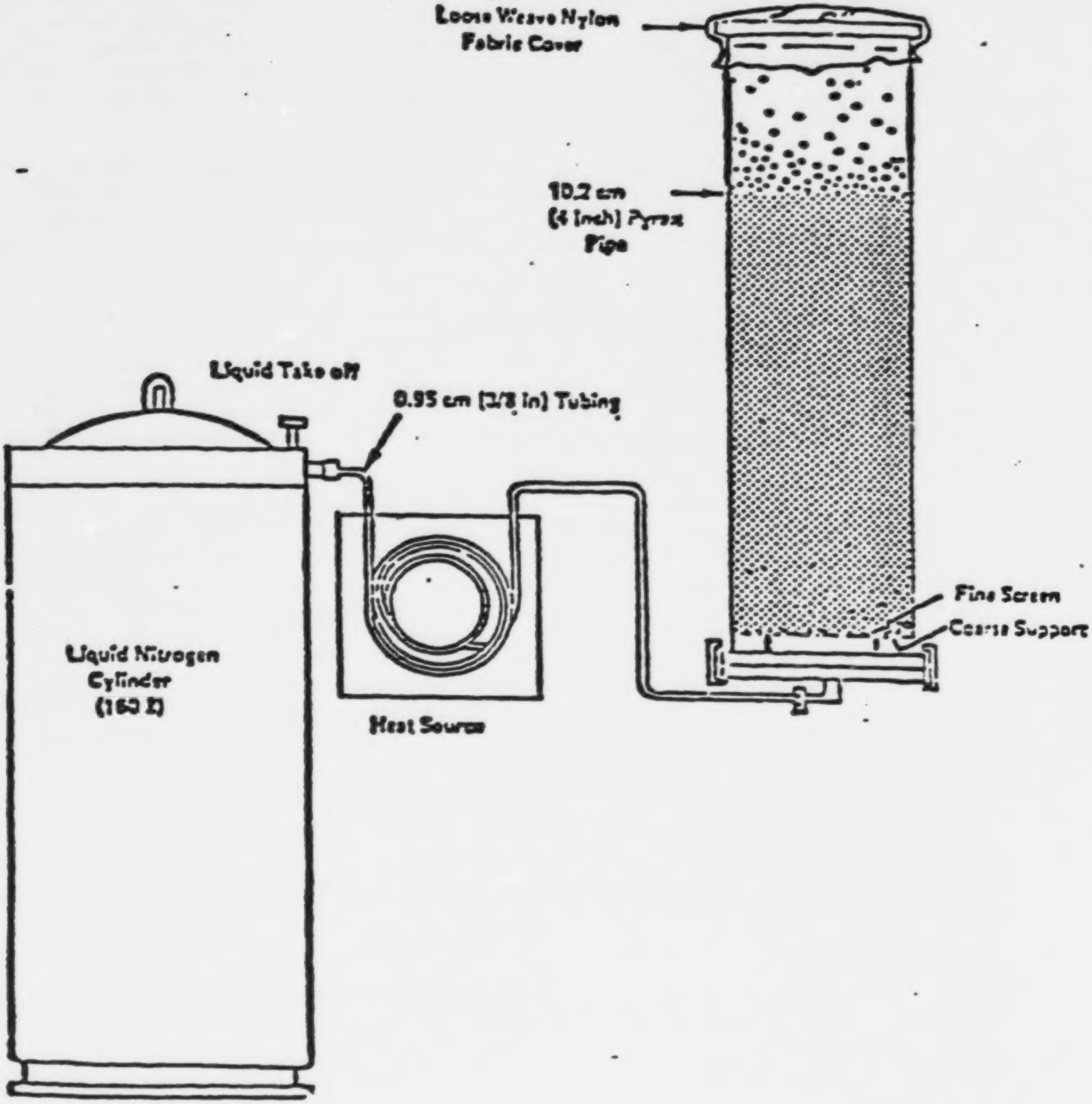
Loose Weave Nylon Fabric Cover
10.2 cm (4 inch) Pyrex Pipe
Liquid Take off
0.95 cm (3/8 in) Tubing
Fine Screen
Coarse Support
Liquid Nitrogen Cylinder (160 l)
Heat Source

Fig. 4 XAD-2 Fluidized-Bed Drying Apparatus

contamination if stored for periods exceeding a few weeks.

If precleaned XAD-2 is not to be used immediately, it shall be stored under distilled-in-glass methanol. No more than two weeks prior to initiation of field sampling, the excess methanol shall be decanted; the XAD-2 shall be washed with a small volume of methylene chloride and dried with clean nitrogen as described in (b) above. An aliquot shall then be taken for the QC contamination check described in (d), below.

If the stored XAD-2 fails the QC check, it may be recleaned by repeating the final two steps of the extraction sequence above: sequential methylene chloride and hexane extraction. The QC contamination shall be repeated after the XAD-2 is recleaned and dried.

(d) QC Contamination Check: The XAD-2, whether purchased, "precleaned", or cleaned as described above, shall be subjected to a QC check to confirm the absence of any contaminants that might cause interferences in the subsequent analysis of field samples. An aliquot of XAD-2, equivalent in size to one field sampling tube charge, shall be taken to characterize a single batch of XAD-2.

The XAD-2 aliquot shall be subjected to the same extraction, concentration, cleanup, and analytical procedure(s) as is (are) to be applied to the field samples. The quantitative criteria for acceptable XAD-2 quality will depend on the detection limit criteria established for the field sampling and analysis program. XAD-2 which yields a background or blank signal greater than or equal to that corresponding to one-half the MDL for the analyte(s) of concern shall be rejected for field use. Note that the acceptance limit for XAD-2 cleanliness depends not only on the inherent detection limit of the analytical method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

8.1.3 Glass Wool

Cleaned by thorough rinsing, i.e., sequential immersion in three aliquots of hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

8.1.4 Water

Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

8.1.5 Silica Gel

Indicating type, 6-16 mesh. If previously used, dry at 175±5C for 2 hr. New silica gel may be used as received.

8.1.6 Crushed Ice

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Place crushed ice in the water bath around the impingers during sampling.

9. SAMPLE RECOVERY REAGENTS

9.1 Acetone

Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

9.2 Hexane

Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

10. PROCEDURE

Caution: Sections 10.1.1.2 and 10.1.1.3 shall be done in the laboratory.

10.1 Sampling

10.1.1 Pretest Preparation

All train components shall be maintained and calibrated according to the procedure described in APTD-0576 unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a precleaned glass container or wrapped hexane-rinsed aluminum foil.

10.1.1.1 Preliminary Determinations

Select the sampling site and the minimum number of sampling points according to EPA Method 1. Determine the stack pressure, temperature, and the range of velocity heads using EPA Method 2; it is recommended that a leak-check of the pitot lines (see EPA Method 2, Sec. 3.1) be performed. Determine the moisture content using EPA Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate-settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, Sec. 3.6; if integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the EPA Method 4 sampling.

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Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

Select a suitable probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min., and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume determined in Section 6.3. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid time-keeping errors.

10.1.1.2 Cleaning Glassware

All glass parts of the train upstream of and including the sorbent module and the first impingers should be cleaned as described in Section 3A of the 1980 issue of "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples."[3] Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

10.1.1.3 Amberlite XAD-2 Resin Trap

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned XAD-2 to fill completely the glass sorbent trap which has been thoroughly cleaned as prescribed and rinsed with hexane. Follow the XAD-2 with hexane-rinsed glass wool and cap both ends. These caps should not be removed until the trap is fitted into the train. See Fig. ② for details. — 1

The dimensions and XAD-2 capacity of the sorbent trap, and the volume of gas to be sampled, should be varied as necessary to ensure efficient collection of the species of interest. Some illustrative data are presented in Table 1.

10.1.2 Preparation of Collection Train

During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until

TABLE 1

SAMPLE SIZE AND FLOW RATE COMPARISON FOR SEVERAL SORBENT TRAP DESIGNS

Trap	Dimensions (mm)		Charge of XAD-2 Resin (g)	Flow Equivalent to 43 cm/sec [a]	Max. Sample Size (cm^3) for Efficient Capture of Following Compounds[b]		
	Depth	Diameter			Octane	Benzene	Phenol
SASS	70	90	130	165 Lpm (5.9 cfm)	150	3.0	240
ADL	70	45	40	40 Lpm (1.5 cfm)	45	0.9	74
Battelle	70	30	19	18 Lpm (0.65 cfm)	22	0.4	35

[a] Upper limit beyond which collection efficiency drops off.

[b] Calculated from V_g^T for 50% breakthrough. Specified value includes a safety factor of 2.

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just prior to assembly or until sampling is about to begin. Caution: Do not use sealant greases in assembling the train.

Place approximately 100 gms of water in each of the first two impingers with a graduated cylinder, and leave the third impinger empty. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Assemble the train as shown in Fig. 1.

Place crushed ice in the water bath around the impingers.

10.1.3 Leak Check Procedures

10.1.3.1 Initial Leak Check

The train, including the probe, will be leak checked prior to being inserted into the stack after the sampling train has been assembled. Turn on and set (if applicable) the heating/cooling system(s) to cool the sample gas yet remain at a temperature sufficient to avoid condensation in the probe and connecting line to the first impinger (approximately 120°C). Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle with a TFE® plug and pulling a 380 mm Hg (12 in. Hg) vacuum. A leakage rate in excees of 4% of the average sampling rate or 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable. Sampling must cease if pressure during sampling exceeds the leak check pressure.

The following leak check instruction for the sampling train described in APTD-0576 (2) and APTD-0581 (4) may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (12 in. Hg) vacuum is reached. Do not reverse the direction of the bypass valve. This will cause water to back up into the probe. If 380 mm Hg (12 in. Hg) is exceeded during the test, either leak check at this higher vacuum or end the leak check as described below and start the test over.

When the leak check is completed, first slowly remove the TFE® plug from the inlet to the probe then immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

10.1.3.2 Leak Checks During a Test

A leak check shall be performed before and after a change of port during a test. A leak check shall be performed before and after a component (e.g., filter or optional water knockout trap) is changed during a test.

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Such leak checks shall be performed according to the procedure given in Section 10.1.3.1 of this method except that it shall be performed at a vacuum equal to or greater than the highest value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller) the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and then correct the volume of gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test.

10.1.3.3 Post-Test Leak Check

A leak check is mandatory at the end of a test. This leak check shall be performed in accordance with the procedure given in Section 10.1.3.1 except that it shall be conducted at a vacuum equal to or greater than the highest value recorded during the test. If the leakage rate if found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller), the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and correct the volume as gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test. 15

10.1.3.4 Correcting for Excessive Leakage Rates

The equation given in Section 11.3 of this method for calculating V_m(std), the corrected volume of gas sampled, can be used as written unless the leakage rate observed during any leak check after the start of a test exceeded L_a, the maximum acceptable leakage rate (see definitions below). If an observed leakage rate exceeds L_a, then replace V_m in the equation in Section 11.3 with the following expression:

$$[V_m - \sum_{i=1}^{n} (L_i - L_a)\theta_i - L_p - L_a)\theta_p]$$

where:

V_m = Volume of gas sampled as measured by the dry gas meter (dscf).

L_a = Maximum acceptable leakage rate equal to 0.00057 m^3/min. (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.

L_p = Leakage rate observed during the post-test leak check, m^3/min (ft^3/min).

L_i = Leakage rate observed during the leak check performed prior to the "i th" leak check (i = 1,2,3...n), m^3/min (ft^3/min).

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θ_i = Sampling time interval between two successive leak checks beginning with the interval between the first and second leak checks, min.

θ_p = Sampling time interval between the last (n th) leak check and the end of the test, min.

Substitute only for those leakages (L_i or L_p) which exceeded L_a.

10.1.3.5 Train Operation

During the sampling run, a sampling rate within 10% of the selected sampling rate shall be maintained. Data will be considered acceptable if readings are recorded at least every 5 min. and not more than 10% of the point readings are an excess of ±10% in and the average of the point readings is within ±10%. During the run, if it becomes necessary to change any system component in any part of the train, a leak check must be performed prior to restarting.

For each run, record the data required on the data sheets. An example is shown in Fig. 4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted.

To begin sampling, remove the nozzle cap, verify (if applicable) that the probe and sorbent module temperature control systems are working and at temperature and that the probe is properly positioned. Position the probe at the sampling point. Immediately start the pump and adjust the flow rate.

If the stack is under significant sub-ambient pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse adjust valve closed.

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath. Also, periodically check the level and zero of the manometer and maintain the temperature of sorbent module at or less than 20°C but above 0°C.

If the pressure drop across the train becomes high enough to make the sampling rate difficult to maintain, the test run shall be terminated unless the replacing of the filter corrects the problem. If the filter is replaced, a leak check shall be performed.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform the post test leak check.*

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*With acceptability of the test run to be based on the same criterion as in 10.1.3.1.

Fig 4

FIELD DATA

PLANT ____________________
DATE ____________________
SAMPLING LOCATION ____________________
SAMPLE TYPE ____________________
RUN NUMBER ____________________
OPERATOR ____________________
BAROMETRIC PRESSURE ____________________
SITE TO BARO ELEVATION (ft) ____________________
CORRECTED B P ____________________
STATIC PRESSURE (P_s) ____________________
FILTER NUMBER(s) ____________________

PROBE LENGTH AND TYPE ____________________
NOZZLE I D ____________________
ASSUMED MOISTURE, % ____________________
SAMPLE BOX NUMBER ____________________
METER BOX NUMBER ____________________
TEMPERATURE METER NO ____________________
THERMOCOUPLE I D NO ____________________
METER ΔH@ ____________________
METER CORRECTION ____________________
C FACTOR ____________________
REFERENCE Δp ____________________
CHEMICAL COND I D NO ____________________

LEAK CK: Initial at ≥15" Hg. CFM ____________________
Final at ______ " Hg. CFM ____________________
Pitot at ≥3" H_2O ____________________

SCHEMATIC OF TRAVERSE POINT LAYOUT
Read and Record All Data
Every ______ Minutes

$$Vm_i = \_\_\_\_\_\_(Tm + 460)\sqrt{\frac{\Delta P_s}{Ts + 460}}$$

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft³		VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
		Desired	Actual		DESIRED	ACTUAL		INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F		XAD-2	

COMMENTS

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10.2 Sample Recovery

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safety handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with hexane-rinsed aluminum foil. Seal off the inlet to the train with a ground glass cap or hexane-rinsed aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area should be clean and enclosed so that the chances of contaminating or losing the sample will be minimized. No smoking shall be allowed.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broker filters, color of the impinger liquid, etc. Treat the samples as follows:

10.2.1 Container No. 1

Either seal the ends of the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

10.2.2 Sorbent Modules

Remove the sorbent module from the train and cap it off.

10.2.3 Cyclone Catch

If the optional cyclone is used, quantitatively recover the particulate into a sample container and cap.

10.2.4 Sample Container No. 2

Quantitatively recover material deposited in the nozzle, probe, transfer line, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with acetone and then hexane three times each and add all these rinses to Container No. 2. Mark level of liquid on container.

10.2.5 Sample Container No. 3

Rinse the back half of the filter holder, the connecting line between the filter and the condenser and the condenser (if using the separate condenser-sorbent trap) three times each with acetone

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and hexane collecting all rinses in Container 3. If using the combined condenser-sorbent trap, the rinse of the condenser shall be performed in the laboratory after removal of the XAD-2. If the optional water knockout trap has been employed, it shall be weighed and recorded and its contents placed in Container 3 along with the rinses of it. Rinse it three times each with acetone, and hexane. Mark level of liquid on container.

10.2.6 Sample Container No. 4

Remove the first impinger. Wipe off the outside of the impinger to remove excessive water and other material, weigh (stem included), and record the weight on data sheet. Pour the contents and rinses directly into Container No. 4. Rinse the impinger sequentially three times with acetone, and hexane. Mark level of liquid on container.

10.2.7 Sample Container No. 5

Remove the second and third impingers, wipe the outside to remove excessive water and other debris, weigh (stem included) and record weight on data sheet. Empty the contents and rinses into Container No. 5. Rinse each with distilled DI water three times. Mark level of liquid on container.

10.2.8 Silica Gel Container

Remove the last impinger, wipe the outside to remove excessive water and other debris, weigh (stem included), and record weight on data sheet. Place the silica gel into its marked container.

11. CALCULATIONS

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

11.1 Nomenclature

G_s = Total weight of chlorinated organic compounds in stack gas sample, ng.

C_s = Concentration of chlorinated organic compounds in stack gas, $\mu g/m^3$, corrected to standard conditions of $20^\circ C$, 760 mm Hg ($68^\circ F$, 29.92 in. Hg) on dry basis.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

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P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/^{o}K-g-mole (21.83 in. Hg-ft^3/^{o}R-lb-mole).

T_m = Absolute average dry gas meter temperature ^{o}K (^{o}R).

T_s = Absolute average stack gas temperature ^{o}K (^{o}R).

T_{std} = Standard absolute temperature, 293^{o}K (68^{o}F).

m_{lc} = Total mass of liquid collected in impingers and silica gel.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

V_m(std) = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

V_w(std) = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by combustion calculation, m/sec (ft/sec).

Y = Meter box correction factor.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

P_w = Density of water, 1 g/ml (0.00220 lb/ml).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

11.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See data sheet (Fig. 4).

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11.3 Dry Gas Volume

Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68±F, 29.92 in. HG)] by using Equation 1.

$$V_m(std) = Y V_m \frac{T_{std} + d}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K_1 V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \qquad (1)$$

where:

K_1 = 0.3855 °K/mm Hg for metric units

= 17.65 °R/in. Hg for English units

11.4 Volume of Water Vapor

$$V_w(std) = m_{lc} \frac{RT_{std}}{M_w \times P_{std}} = K_2 m_{lc} \qquad (2)$$

where:

K_2 = 0.00134 m^3/ml for metric units

= 0.0472 ft^3/ml for English units

11.5 Moisture Content

$$B_{ws} = \frac{V_{w(std)}}{V_m(std) + V_{w(std)}} \qquad (3)$$

If liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

11.6 Percent Isokinetic Sampling

$$I = \frac{100\ T_s\ [K_4\ Mlc + (Vm\ Km)\ (P_{bar} + \Delta H/13.6)]}{60\ \theta_{vs}\ P_s\ A_n} \qquad (4)$$

where:

K_4 = 0.003454 mm Hg - m^3/ml - °K for metric units

= 0.002669 in Hg - ft^3/ml - °R for English units

11.7 Concentration of Chlorinated Organic Compounds in Stack Gas

Determine the concentration of chlorinated organic compounds in the stack gas according to Equation 5.

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$$C_s = K_5 \frac{G_s}{V_m(std)} \qquad (5)$$

where:

$$K_5 = 35.31\ ft^3/m^3$$

12. QUALITY ASSURANCE (QA) PROCEDURES

The positive identification and quantification of specific compounds in this assessment of stationary conventional combustion sources is highly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in this section were designed to monitor the performance of the sampling methods and to provide information to take corrective actions if problems are observed.

Field Blanks

The field blanks should be submitted as part of the samples collected at each particular testing site. These blanks should consist of materials that are used for sample collection and storage and are expected to be handled with exactly the same procedure as each sample medium.

Blank Train

For each series of test runs, set up a blank train in a manner identical to that described above, but with the probe inlet capped with hexane-rinsed aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Sec. 7.2.

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APPENDIX B

SAMPLE CALCULATION OF MINIMUM SAMPLE VOLUME

MINIMUM SAMPLE TIME CALCULATIONS

A = Analytical MDL = 400×10^{-12} g from Robert Harless, ESML

B = Percent of sample used per run = 10 percent

C = Sample recovery (40-100 percent), choose 50 percent

D = Allowable stack emissions = 1-100 ppt by volume

V = Required sample volume (1)

Molecular weight of 2,3,7,8-TCDD = 320 g/gmole

1 ppt (volume basis) = $1 \times 10^{-12} \times 320$ g/gmole x 1 gmole/22.41

$= 1.42 \times 10^{-11}$ g/1

Sufficient sample is needed on both front and back half to be seen at MDL. Assume TCDD equally distributed between front and back halves.

$$\overset{(A)}{\text{MDL}} = \text{Sample (v) volume} \times \overset{(D)}{\text{concentration}} \times \overset{(B)}{\frac{10}{100}} \times \frac{1}{2} \times \overset{(C)}{\frac{50}{100}}$$

$$\text{Sample volume} = \frac{A}{D} \times \frac{100}{B} \times 2 \times \frac{100}{C}$$

= 1127 1

= 39 cu ft

Assume sample rate = 0.5 cfm

$$\text{Minimum sample time} = \frac{39\ \text{ft}^3}{1/2\text{ft}^3\text{mn}} = 80\ \text{mins}$$

= sample volume/sample rate = 39 cu ft/0.5 cfm = 80 min

It is generally desirable to achieve 3-4 times the MDL for the purposes of analytical certainly. Therefore, choose a sampling time of 4 hours for the test program.

APPENDIX C

DIRECTIONS FOR DIOXIN SAMPLE SHIPMENT

RADIAN
CORPORATION

Sample Control Center
National Dioxin Study

July 1984

DIOXIN SAMPLE DOCUMENTATION AND SHIPMENT INSTRUCTIONS FOR SAMPLERS

Instructions for Completing DSR Form

A separate Dioxin Shipment Record (DSR) form is to be completed for each shipment of samples to a laboratory. For samples going to Troika laboratories, use the SCC DSR provided by the Sample Control Center.

First, enter the Episode number on the top right corner of the DSR form, where indicated. The Episode number is the identifying number that was assigned by SCC at the time the sampling was scheduled. This is followed by the Batch number, which is assigned by the sampler when samples are packed for shipment to the laboratory(s).

The Batch number represents one shipment of samples from one specific location to one laboratory on one day, and is assigned sequentially. For example, the first shipment of samples in an Episode would be identified as Batch #1, the second shipment would be Batch #2, etc. When sampling occurs over several days, care must be taken not to repeat Batch numbers within the Episode.

The use of Batch numbers allows for identification of groups of samples within an Episode that are shipped to different laboratories and/or that are shipped on different days. The Batch number may also be used to signify a group of samples collected at a specific location within the overall site perimeter, should the site encompass a large geographical area.

Next, complete header information, excluding the grey areas on the top right of the form.

Along with the DSR forms, the Region has two sets of labels bearing sample numbers. Two strips of labels containing the same series of 24 Sample numbers are provided for use in labeling the sample bottles and the outer metal cans in which samples are packaged for shipment. The same numbered label must be placed on both the sample bottle and the outer metal can. In order to protect the labels from water or solvent attack, labels on both the sample container and the outer metal can should be covered with clear, waterproof tape.

Enter the Sample numbers (from the labels) on the lower left side of the DSR form, where indicated. Record all Sample numbers for samples included within the Batch shipment. (Extra numbered labels from the original strips of 24 should be discarded and new strips of labels should be used for the next Batch of samples.)

For each sample, indicate sample matrix and description by checking the appropriate box in each category. There is also a block for indicating that additional analysis is required for a sample. Check this block, if appropriate, and specify type of additional analysis. (Any additional analytical work must be approved by Office of Water and requested through SCC at the time sampling is scheduled, to ensure that proper arrangements can be made in advance to accommodate the request.)

On the SCC DSR form, the bottom two copies of the completed DSR (pink and gold copies) must be included with the sample shipment to the laboratory. The DSR, as well as chain-of-custody documentation accompanying the sample shipment, should be enclosed in a clear plastic bag and securely taped to the underside of the lid of the shipping cooler.

Following sample shipment, distribute remaining DSR copies as follows:

- Mail the top (white) copy to SCC at the address shown on the top of the DSR form.

- Mail the second (green) copy of the SCC DSR to Duluth ERL. Mailing address: USEPA ERL-Duluth, 6201 Congdon Blvd., Duluth, Minnesota 55804; Attn: Darcy Johnson.
- The third (yellow) copy of DSR form is retained by the sampler as the Region's file copy.

Procedures for Coordinating Sample Shipment

Immediately following sample shipment, call SCC and provide the following information:

- Sampler name
- Episode number
- Batch number(s)
- Sample numbers for samples included in each Batch
- Date of shipment
- Courier name and airbill number
- Type of shipment (e.g., overnight, two-day)
- Laboratory samples shipped to
- Any irregularities or anticipated problems with the samples
- Status of sampling project (e.g., final shipment, update of future shipping schedule)

SCC notifies the laboratory that samples are in transit and confirms arrival of the samples in good condition at the receiving laboratory. SCC assists in resolution of any problems concerning the samples, coordinating with the appropriate Regional or sampling personnel.

Upon sample receipt, the laboratory completes designated sections of the DSR, recording date of sample receipt and sample condition, signs the DSR, and returns a copy to SCC. SCC retains the laboratory-signed DSR copy as written confirmation of sample receipt.

Chain-of-Custody Requirements

Three types of chain-of-custody documents are utilized: sample tags, Chain-of-Custody Records and custody seals. These documents are available through the Regions.

A sample tag should be completed and securely attached to each sampling container. The information to be recorded on an EPA Sample Tag includes:

- Sample Number – The unique identification number used to document that sample.
- Episode Number – The unique number assigned by SCC to that sampling event.
- Batch Number – The number assigned by the sampler to that shipment.
- Project Code – The number assigned by EPA to that project.
- Station Number – A two-digit number assigned by the Sampling Team Coordinator and listed in the project plan.
- Date – A six-digit number indicating the month, day and year of collection.
- Time – A four-digit number indicating the military time of collection.
- Station Location – The sampling station description from the project plan.
- Sampler – Each sampler's name.
- Tag Number – A serial number preprinted on each tag.
- Remarks – The samplers' recorded pertinent observations.

Enter the sample number, Episode number, Batch number, courier name and airbill number, and other pertinent information in the tag's "Remarks" section. Spaces are designated for project code, station number, collection date and time, station location, and sampler name(s). The sample tag number is preprinted on the tag. Additionally, the sample tag contains spaces for indicating whether the sample is a grab or composite, if a preservative was used, and the analytical parameters required for that sample (enter "dioxin" on blank line provided).

After attaching sample tags and packaging, samples are to be shipped with an accompanying Chain-of-Custody Record to maintain official custody of samples from the time of collection onward, in accordance with Agency enforcement requirements. For Agency purposes, a sample is considered to be in an individual's custody if the following criteria are met: it is in your possession or it is in your view after being in your possession; it was in your possession and then locked up or transferred to a designated secure area. The sampler is responsible for the care and custody of the samples collected until they are shipped.

A separate Chain-of-Custody Record should accompany each sample shipment to a laboratory. Record sample numbers, sample tag numbers and analytical parameters for each sample on the Chain-of-Custody Record, using indelible ink. Corrections to the custody form are to be made by drawing a line through and initialing the error, and then entering the correct information. After completion, sign and date the custody form to officially relinquish custody of the samples for shipment.

The original custody record should be enclosed in plastic (with the Dioxin Shipment Record) and securely taped to the underside of the cooler lid. The copy may be retained for Regional records.

Shipping coolers should then be secured and sealed with a custody seal for shipment to the laboratory. Custody seals should be placed across the cooler opening so that the cooler cannot be opened without breaking the seal. As long as the custody form is sealed inside the sample cooler and the custody seal remains intact, commercial carriers are not required to sign off on the custody form.

The laboratory representative who accepts the incoming sample shipment will sign and date the Chain-of-Custody Record to acknowledge receipt of the samples, completing the sample transfer process. From that point, the laboratory maintains internal log books and records that provide a custody record throughout sample preparation and analysis.

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DIOXIN SAMPLE NUMBER

D	A	0	0	0	1	0	1
SIGNIFIES DIOXIN SAMPLE	REGIONAL CODE	NON-REPEATING NUMERICAL SEQUENCE				REPEATING NUMERICAL SEQUENCE (REPEATS 01 THR 24 TO CORRESPO WITH BATCH SAM COLLECTION)	

REGION CODES

Region	Code
I	A
II	B
III	C
IV	D
V	E
VI	F
VII	G
VIII	H
IX	Y
X	J

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EPA "TROIKA" LABORATORIES FOR SHIPMENT OF NATIONAL DIOXIN STUDY SAMPLES

USEPA ERL - Duluth
6201 Congdon Blvd.
Duluth, MN 55804
Attention: Darcy Johnson

USEPA ECL Toxicant Analysis Center
Building 1105
Bay St. Louis, MS 39529
Attention: Danny McDaniel

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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2.

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Quality Assurance Project PLan

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7. AUTHOR(S)
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J.T. Bursey

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231-056-12-17

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Radian Corporation
P.O. Box 13000
Research Triangle Park, NC 27709

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68-03-3148

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Environmental Protection Agency
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
Research Triangle Park, NC 27711

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Quality Assurance Project Plan

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
EPA Project Officers: William H. Lamason and Donald Oberacker

16. ABSTRACT

The objective of Tier 4 of the National Dioxin Study is to determine if combustion devices are significant sources of dioxin emissions. This project plan describes the quality assurance and quality control activities associated with emission tests to be conducted at twelve (12) sites. The tests will involve determination of of dioxin concentrations and mass flow rates at the outlet of the combustion device and/or any air pollution control equipment. Flue gas combustion parameters (CO, CO_2, O_2, SO_2, NO_x, and total Hydrocarbons) will be monitored and samples for dioxin precursor analysis will be collected. Equipment calibration, sample custody, data reduction, and reporting requirements are discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Dioxin Combustion processes Qaulity Assurance Sampling Chemical Analysis 2,3,7,8, - tetrachlorodibenzo-p-dioxin TCDD, PCDD	National Dioxin Study Air Pollution Measurement	13B

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